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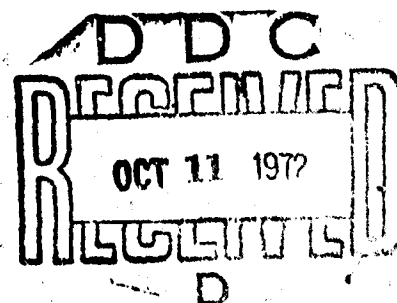
PREDICTION OF EXHAUST EMISSIONS FROM PRIME MOVERS AND SMALL HEATING PLANT FURNACES

by

S. C. Sorenson
J. J. Stukel
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13. ABSTRACT This report is the result of an investigation of the possibilities of predicting the exhaust emissions from various types of prime-movers and small heating plant furnaces. The prime-movers investigated include spark ignition engines, compression ignition engines, and gas turbines. Based on a survey of currently available literature and data, it was determined that carbon monoxide and oxides of nitrogen correlate reasonably well with basic engine variables for spark ignition and compression ignition engines. Hydrocarbon emissions in these engines do not correlate well, even though some consistent effects of variables were found for spark ignition engines. Smoke emissions from compression ignition engines did not correlate with engine variables. Recent correlations of various smoke measuring devices are presented. Gas turbine emission correlation attempts were unsuccessful due, to some extent to lack of meaningful data to accompany emissions data. Correlation relating emissions of sulfur dioxide and total oxides of nitrogen for small heating plant furnaces with the gross heat input for oil-, coal-, and gas-fired units were established. In addition, equations used to calculate theoretical carbon dioxide emissions for gaseous, liquid, and solid fuels are presented. Attempts to correlate sulfur trioxide, hydrocarbons, particulates, and carbon monoxide emissions with process variables were unsuccessful. Emission factors for these pollutants are presented.			
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July 1972

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FOREWORD

The investigation presented in this report was supported by the Electromechanical Systems Laboratory, U.S. Army Construction Engineering Research Laboratory (CERL), Champaign, Illinois. The work was carried out at the Department of Mechanical and Industrial Engineering, University of Illinois, Urbana. Mr. R. G. Donaghy was Chief of the Electromechanical Systems Laboratory, and Colonel E. S. Townsley was Director of CERL during the course of this study. This investigation was funded under Contract No.: DACA 23-70-C-0080, project 21 02020 08-7035 P2270.4-251 S11-205 07670101, "Engineering Criteria for Design and Construction Technical Support."

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PREDICTION OF EXHAUST EMISSIONS FROM PRIME MOVERS AND SMALL HEATING PLANT FURNACES

PART I: INTRODUCTION

Background

Due to increased concern on the part of the general public as to the quality of the environment, new air quality standards are being enacted. To meet these standards with existing and future installations and equipment, it is necessary to know the nature and quantity of emissions from various prime movers and small heating plant furnaces which are a part of these installations and equipment. The National Air Quality Standards were established in April 1971. They can be located in the Federal Register, Vol. 36, No. 84 of 30 April 1971.

In the past few years, a substantial amount of information has been generated and published concerning the nature and quantity of emissions from prime movers and small heating plant furnaces. This information, however, has not been collected and investigated as to the possibility of its use to make generalized prediction of the emissions from these various devices. This report will be used by designers as general background material in preparing criteria and preliminary designs.

Purpose and Scope

The purpose of this study was to develop a model to predict the constituents of exhaust gases from diesel and gas engines, gas turbines, and small-to-medium size heating plant furnaces under various load conditions and using various fuels. A survey of currently available emission data from various sources was undertaken and the results correlated where possible to develop a series of models for specific pollutants. Pollutants examined in the modeling studies were oxides of nitrogen, hydrocarbons, carbon monoxide, carbon dioxide, sulfur dioxide, and particulates. The models presented reflect (1) equipment design; (2) equipment operating procedures; and (3) the age and condition of the equipment. The results outputted from this model will be input to other models which will actually predict the ambient pollution levels created by each of these items of equipment.

PART II: SPARK IGNITION ENGINES

Carbon Monoxide Emissions

On a mass basis, carbon monoxide (CO) is the largest portion of total emissions from spark ignition engines. This is especially true for typical constant speed variable load operation in which engines run under conditions which produce large amounts of CO. As illustrated in Fig. 1, CO emissions are essentially determined by the fuel-air mixture of the engine. The curves in this figure were obtained from the spark ignition engine emissions references given in Bibliography. If the mixture contains more fuel than the stoichiometric amount, CO emissions will be significant, while, if the mixture contains less than the chemically correct amount of fuel, the CO emissions will be low and generally insignificant.

For fuel rich combustion, the carbon monoxide emissions can be well determined from the overall engine fuel-air ratio. This can be expressed in terms of the equivalence ratio ϕ

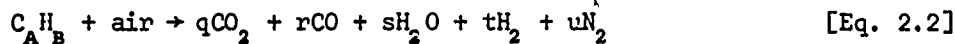
$$\phi = \frac{FA|_{\text{actual}}}{FA|_{\text{stoichiometric}}} \quad [\text{Eq. 2.1}]$$

where

$FA|_{\text{actual}}$ = fuel-air ratio on which the engine is operating--lb/lb

$FA|_{\text{stoichiometric}}$ = chemically correct or stoichiometric fuel-air ratio--lb/lb

For fuel rich combustion, ϕ is greater than one and the percent CO can be calculated for the chemical reaction of an arbitrary fuel, $C_A H_B$, and air, as given in Eq. 2.2.



Balancing the chemical equation for various equivalence ratios leads to the following expressions for the coefficients of the products in Eq. 2.2.

$$q = A - \left(\frac{2A + B/2}{1 + 1/K} \right) \left(1 - \frac{1}{\phi} \right) \quad [\text{Eq. 2.3}]$$

$$r = \left(\frac{2A + B/2}{1 + 1/K} \right) \left(1 - \frac{1}{\phi} \right) \quad [\text{Eq. 2.4}]$$

$$s = \frac{B}{2} - \left(\frac{2A + B/2}{K + 1} \right) \left(1 - \frac{1}{\phi} \right) \quad [\text{Eq. 2.5}]$$

$$t = \left(\frac{2A + B/2}{K + 1} \right) \left(1 - \frac{1}{\phi} \right) \quad [\text{Eq. 2.6}]$$

$$u = \frac{3.76}{\phi} \left(A + \frac{B}{4} \right) \quad [\text{Eq. 2.7}]$$

where

$K = \text{ratio of CO to H}_2 \text{ in products} = t/r$

Typical values of K run between 1.8 and 2.5 (Ref. 10).

The percent of CO in the exhaust of a spark ignition engine can then be determined by the following relations.

$$\text{On a dry basis, percent CO} = \frac{r}{q + r + t + u} \quad [\text{Eq. 2.8}]$$

$$\text{On a wet basis, percent CO} = \frac{r}{q + r + s + t + u} \quad [\text{Eq. 2.9}]$$

Figure 2 shows a series of predicted curves of CO, CO₂, and H₂ emissions from a spark ignition engine as a function of equivalence ratios for a typical fuel, C_nH_{2n}, and varying ratios of CO to H₂.

It should be re-emphasized that the above relations are only valid for the case in which the fuel air equivalence ratio is greater than one. As mentioned previously, for lean mixtures, the CO emissions are less than one percent and are insignificant compared to emissions from rich mixtures.

Oxides of Nitrogen Emissions

As was the case with carbon monoxide, the emissions of oxide of nitrogen (NO_x) are strongly dependent on the overall fuel-air ratio supplied. In addition, NO_x emissions are also dependent on peak cycle temperatures which, in turn, are functions of the intake manifold pressure, spark timing, and compression ratio. Typical spark ignition engines operate with a compression ratio of 7:1 to 9:1 and the data in the literature indicated that, although there is an effect of compression ratio, within this range of compression ratios, the effect is not appreciable (Ref. 11). The effect of compression ratio was consequently neglected in the correlation of NO_x data.

There is a substantial amount of data in the literature concerning NO_x emissions, usually accompanied by rather complete engine data. Figure 3 shows data from a typical source. These data show the combined effects of air-fuel ratio, spark timing, and intake manifold pressure on NO_x emissions (Ref. 16). From similar plots from other references, it was found that curves of NO_x emissions as a function of air-fuel ratio are very similar in shape to the normal distribution or Gaussian curve. The NO_x emissions were then fit to a Gaussian-type curve in which the parameters were found to be functions of the engine variables of intake manifold pressure and spark timing. The Gaussian curve has the general form:

$$f(x) = A e^{-1/2[(x-c)/B]^2} \quad [\text{Eq. 2.10}]$$

The parameter A is equal to the maximum value of $f(x)$, B is related to the half-width of the curve, and C is the value of x at which the maximum value of $f(x)$ occurs. The equation for NO_x concentration as a function of engine variables then has the form

$$NO_x = [NO_x]_{max} \exp \left\{ -\frac{1}{2} \left[\frac{AF - AF|_{max}}{B} \right]^2 \right\} \quad [Eq. 2.11]$$

where

NO_x = NO_x concentration--parts per million on a dry volume basis

$NO_x|_{max}$ = maximum NO_x concentration

AF = engine operating air fuel ratio--lb/lb

$AF|_{max}$ = air fuel ratio at which the maximum NO_x concentration occurs--lb/lb

The parameter B was determined from the available data and was found to be essentially independent of the engine operating conditions. The best fit to the experimental data, as determined by visual interpretation, was found with a value of $B = 2.0$.

The maximum value of NO_x was found to be an approximately linear function of spark timing and fuel-air ratio. Figures 4 and 5 show experimental data curves of maximum nitric oxide concentration as a function of intake manifold pressure and spark timing. The equation obtained is

$$NO_x|_{max} = -1215 + 102.31(p_{int}) + 73.04 (\text{spark}) \quad [Eq. 2.12]$$

where

p_{int} = intake manifold pressure--inches mercury absolute

spark = spark timing--degrees before top dead center

A similar procedure was followed for the air-fuel ratio at which the maximum concentration of NO_x occurred. These results are shown in Figs. 6 and 7. The equation obtained is

$$AF|_{max} = 12.98 + 0.0814(p_{int}) + 0.0245 (\text{spark}) \quad [Eq. 2.13]$$

The effects of spark timing and intake pressure on $AF|_{max}$ were not as pronounced as in the case of $NO_x|_{max}$. Some of this may be due to variation in air-fuel ratios between different references. It was observed, however, that, for a consistent set of data from one reference, the air fuel ratio of maximum NO concentration did vary with spark timing and intake manifold pressure. Consequently, it is believed that these effects are realistic.

The model for NO_x emissions then gives NO_x emissions on a dry volume basis as a function of air-fuel ratio, intake manifold pressure, and spark timing.

To summarize, the NO_x model consists of the following equations,

$$\text{NO}_x = [\text{NO}_x]_{\max} \exp \left\{ -\frac{1}{2} \left[\frac{\text{AF} - \text{AF}_{\max}}{2} \right]^2 \right\} \quad [\text{Eq. 2.11}]$$

$$[\text{NO}_x]_{\max} = -1215 + 102.31(p_{\text{int}}) + 73.04 (\text{spark}) \quad [\text{Eq. 2.12}]$$

$$\text{AF}_{\max} = 12.98 + 0.0814(p_{\text{int}}) + 0.0245 (\text{spark}) \quad [\text{Eq. 2.13}]$$

Figures 8, 9, and 10 show typical results from the model for different values of air-fuel ratio, intake manifold pressure, and spark timing.

Hydrocarbon Emissions

The most important variable affecting hydrocarbon emissions from spark ignition engines is the air-fuel ratio. Figure 11 shows typical hydrocarbon levels for a variety of engines and operating conditions. The curves in this figure were obtained from the spark ignition engine references given in Bibliography. Figure 11 shows the wide variety of hydrocarbon production response which can be obtained simply by changing engine geometry and operating conditions. The hydrocarbon concentrations are given in parts per million carbon as measured with a flame ionization detector. These concentrations can be converted to parts per million n-hexane by dividing by a factor of 6. Concentrations measured with non-dispersive infra-red analyzers were converted to equivalent measurements from a flame ionization detector by multiplying by an average correction factor. By nature of its operation, the non-dispersive infra-red analyzer has about one-half the response of a flame ionization detector (Ref. 11).

In addition to air-fuel ratio, spark timing, compression ratio, and engine speed were all found to have an effect on hydrocarbons. Consequently, attempts were made to correct emissions to a common condition of MBT (maximum brake torque spark timing), 8:1 compression ratio, and 1000 rpm. This was done by assuming that the effects of the variables are linear and determining average correction factors (Refs. 13,17,18). These were found to be:

Compression ratio (CR)

$$\frac{\Delta \text{HC}}{\Delta \text{CR}} = +300 \frac{\text{ppmc}}{\text{CR}} \quad [\text{Eq. 2.14}]$$

Engine speed (N)

$$\frac{\Delta \text{HC}}{\Delta \text{N}} = -0.65 \frac{\text{ppmc}}{\text{rpm}} \quad [\text{Eq. 2.15}]$$

Spark timing (Spk)

$$\frac{\Delta \text{HC}}{\Delta \text{Spk}} = +20 \frac{\text{ppmc}}{\text{deg}} \quad [\text{Eq. 2.16}]$$

where

ppmc = hydrocarbon concentration in parts per million carbon on a dry volume basis

and

Spk = degrees of spark advance from MBT timing

It should be pointed out that the above effects will vary from engine to engine and are most likely interrelated. The results, though approximate, do give an indication of magnitude of the effects of the above variables.

Figure 12 shows the results of these corrections for conditions in which MBT timing was known. As can be readily seen, the correlation is not very good; at a typical value of air-fuel ratio, the lowest observed value is about one-third of the highest value shown. This lack of correlation is not surprising when one looks at the formation mechanism for exhaust hydrocarbons. The generally accepted mechanism by which hydrocarbons appear in exhaust gases of spark ignition engines is that of wall quenching (Ref. 12). The cold walls of the combustion chamber extinguish the flame and some of the hydrocarbons left when quenching occurs are then exhausted with the rest of the combustion gases. Thus, the formation is sensitive to the physical design of the combustion chamber as has been verified in the literature (Refs. 13,14,15). A much more sophisticated model, therefore, is required in order to do a more accurate job of predicting exhaust hydrocarbons. Such a model is not currently available.

Oxides of Sulfur

As indicated in Reference 7, the emission of sulfur oxides can be calculated from the amount of sulfur in the fuel. A method for calculating these emissions is outlined in Part V of this report. Emissions of sulfur from spark ignition engines, compression ignition engines, and gas turbines is not important because of the low levels of sulfur in fuels for these engines (Ref. 7). Typical values are 0.04 percent for spark-ignition engines (Ref. 10), 0.37 percent for diesel engines (Ref. 7), and 0.4 percent for turbines (Ref. 10).

PART III: COMPRESSION IGNITION ENGINES

Correlation of Performance with Fuel-Air Ratio

In a compression ignition (CI) engine, the speed and load are controlled by varying the rate of fuel flow to the engine at an essentially fixed air flow rate. Therefore, the fuel-air ratio† is a direct measure of the output of a (CI) engine. This is borne out by Fig. 13 which shows a plot of indicated mean effective pressure (IMEP) vs. fuel-air ratio for various four-stroke engine types. Included are data for precombustion chamber engines and direct injection engines, both turbocharged and normally aspirated, running over a wide range of speeds (Refs. 6,10,19). The data for the turbocharged engines may be corrected to an intake manifold pressure of 29.92 inches of mercury absolute. Figure 14 shows the ratio of IMEP at 29.92 inches of mercury to IMEP at turbocharged conditions as a function of the ratio of inlet manifold pressure to 29.92 inches of mercury for various fuel-air ratios. The resulting correlation is given below.

$$\frac{\text{IMEP}_C}{\text{IMEP}_{TC}} = \left(\frac{P_{TC}}{29.92} \right)^{-0.747} \quad [\text{Eq. 3.1}]$$

where

IMEP_C = indicated mean effective pressure in psi corrected to an intake pressure of 29.92 inches of mercury absolute

IMEP_{TC} = indicated mean effective pressure at turbocharged conditions--psi

P_{TC} = intake manifold pressure at turbocharged conditions--inches of mercury absolute

The final correlation obtained is that of IMEP corrected to an intake pressure of 29.92 inches of mercury absolute as a function of fuel-air ratio. The results obtained for a variety of engine types and speeds is shown in Fig. 15. The curve shown in Fig. 15 is a least squares polynomial which was fit to the data and is given below:

$$\text{FA} = 2.41 \times 10^{-3} + 1.66 \times 10^{-4} (\text{IMEP}_C) + 1.25 \times 10^{-6} (\text{IMEP}_C)^2 \quad [\text{Eq. 3.2}]$$

where

FA = fuel-air ratio--lb fuel/lb air

†For the four-stroke engine, the overall fuel-air ratio is the pertinent variable while, in the case of the two-stroke engine, the variable of interest is the trapped fuel-air ratio.

The equation is given with corrected indicated mean effective pressure as the independent variable. This makes it possible to determine the fuel-air ratio necessary to operate an engine at a given load (IMEP). The corresponding fuel-air ratio can then be correlated with certain emissions from a compression ignition engine.

The indicated mean effective pressure for an engine may be determined from the engine speed, displacement, and horsepower in the following manner:

$$\text{IMEP} = \text{BMEP} + \text{FMEP} \text{---psi} \quad [\text{Eq. 3.3}]$$

BMEP = brake mean effective pressure---psi

FMEP = friction mean effective pressure---psi

Brake mean effective pressure can be calculated using the following relation

$$\text{BMEP} = \frac{\text{BHP} \times (396,000)(a)}{D \times N} \text{---psi} \quad [\text{Eq. 3.4}]$$

BHP = brake horsepower

D = engine displacement---inches³

N = engine speed---rpm

a = 2 for a four-stroke engine

a = 1 for a two-stroke engine

The friction mean effective pressure of an engine is usually not known. However, a correlation of FMEP with engine parameters has been obtained by Taylor and Taylor (Ref. 1) and may be used to estimate FMEP for a given engine. This correlation is given below:

$$\text{FMEP} = \text{FMEP}|_0 + x(p_c - p_i) + y(\text{IMEP} - 100) \quad [\text{Eq. 3.5}]$$

where

$$\text{FMEP}|_0 = 8 + 0.967(S_p/100) + 0.00607(S_p/100)^2 \quad [\text{Eq. 3.6}]$$

$$S_p = \frac{SN}{6} \text{ piston speed---ft/min} \quad [\text{Eq. 3.7}]$$

$$x = 1 - 6.74 \cdot 10^{-5} \left[\frac{B^2}{LD_i} \frac{NS}{\sqrt{T_i}} \right] \text{ for a 4-stroke engine} \quad [\text{Eq. 3.8}]$$

$$x = 0.0 \text{ for a 2-stroke engine}$$

$$y = 0.012 + 1.6 \times 10^{-5} (S_p) \quad [\text{Eq. 3.10}]$$

p_e = exhaust pressure--psia

p_i = intake pressure--psia

S_p = piston speed--ft/min

S = stroke--inches

N = engine speed--rpm

B = bore--inches

L = valve lift--inches

D_i = intake valve diameter--inches

T_i = intake temperature--°R

Values of x for a typical four-stroke engine range from 0.8 at low speeds to 0.2 at high speeds.

Carbon Monoxide Emissions

Fuel-air ratio was found to be the engine variable which had the largest effect on carbon monoxide emission levels. While it is recognized that other engine variables may have an effect on carbon monoxide emissions, the data available in the literature at the present time are not sufficient to correlate these effects. Consequently, carbon monoxide emissions have been correlated solely as a function of fuel-air ratio.

Figure 16 shows typical carbon monoxide emissions as a function of engine fuel-air ratio for a variety of commercial engines. The data in this figure were obtained from the compression ignition engine references given in Bibliography. It can be seen that precombustion chamber engines run with lower levels of carbon monoxide than direct injection engines at high fuel-air ratios (high loads), while the reverse is true at low fuel-air ratios. For the purposes of correlating carbon monoxide emissions as a function of fuel-air ratio, least squares polynomials were fit to average carbon monoxide vs. fuel-air ratio curves for both direct injection engines and precombustion chamber engines. The results obtained are given in Eqs. 3.11 and 3.12 below and are shown graphically in Fig. 17.

For direct injection engines:

$$\begin{aligned} CO = & 1415.0 - 0.7352 \times 10^5 (FA) + 0.2054 \times 10^6 (FA)^2 \\ & + 0.3550 \times 10^8 (FA)^3 \end{aligned} \quad [\text{Eq. 3.11}]$$

For precombustion chamber engines:

$$\begin{aligned} CO = & 1345.0 - 0.1969 \times 10^6 (FA) + 0.3313 \times 10^7 (FA)^2 \\ & - 0.1167 \times 10^8 (FA)^3 \end{aligned} \quad [\text{Eq. 3.12}]$$

where

CO = parts per million carbon monoxide on a dry volume basis

FA = fuel-air ratio--lb/lb

As discussed previously, the fuel-air ratio for a CI engine correlates well with indicated mean effective pressure. Thus, the carbon monoxide emissions can be correlated directly with engine output. This correlation is given by the following relations:

$$\text{IMEP}_C = \text{IMEP}(p_{i_{nt}}/29.92)^{-0.747} \quad [\text{Eq. 3.13}]$$

For the direct injection engines:

$$\begin{aligned} \text{CO} = & 1251.7 - 15.711(\text{IMEP}_C) + 0.0104(\text{IMEP}_C)^2 \\ & - 2.568 \times 10^{-3}(\text{IMEP}_C)^3 + 2.275 \times 10^{-5}(\text{IMEP}_C)^4 \end{aligned} \quad [\text{Eq. 3.14}]$$

For precombustion chamber engines:

$$\begin{aligned} \text{CO} = & 3099 - 31.85(\text{IMEP}_C) - 0.9251(\text{IMEP}_C)^2 \\ & + 1.544 \times 10^{-3}(\text{IMEP}_C)^3 \end{aligned} \quad [\text{Eq. 3.15}]$$

where

CO = parts per million carbon monoxide on a dry volume basis

IMEP_C = corrected engine indicated mean effective pressure--psi

IMEP = actual engine indicated mean effective pressure--psi

$p_{i_{nt}}$ = intake manifold pressure--inches mercury absolute

These equations are presented graphically in Figs. 18 and 19, which show exhaust concentrations of carbon monoxide as a function of actual indicated mean effective pressure for various intake manifold pressures.

Oxides of Nitrogen Emissions

As is the case with carbon monoxide emissions, the most important variable affecting the level of oxides of nitrogen (NO_x) emissions is the fuel-air ratio. Figures 20 and 21 show emissions of oxides of nitrogen from precombustion chamber and direct injection engines as a function of fuel-air ratio. The data in this figure were obtained from the compression ignition engine references given in Bibliography. It can be seen that NO_x emissions fall into two distinct ranges, with the precombustion chamber engines having inherently lower NO_x emissions throughout the range of fuel-ratios. Precombustion chamber engines are especially superior in the range of high fuel-air ratios; i.e., high loads. The available data on two-stroke diesel engines indicate that NO_x emissions

throughout the range of fuel-ratios. Precombustion chamber engines are especially superior in the range of high fuel-air ratios; i.e., high loads. The available data on two-stroke diesel engines indicate that NO_x emissions fall within the range shown in Figs. 20 and 21 when the trapped fuel-air ratio is used.

Other engine variables have an effect on NO_x emissions from CI engines. For example, Fig. 22 shows the effect of changing ignition timing in a particular precombustion chamber and a particular direct ignition engine (Ref. 20). It can be seen that the direct injection engine is much more sensitive to timing than the prechamber engine. While it is recognized that injection timing may have an appreciable effect on NO_x emissions, very few of the data on NO_x emissions are accompanied by timing data and, so, a meaningful correlation of the effect of injection timing is not possible at the present time.

Engine speed is another variable which may have an effect on NO_x emissions. The data in the literature, however, appear contradictory on this point, with some engines showing an appreciable effect while others show a negligible effect. This is probably due to differences in the individual injection systems and combustion chamber designs. Again, because of lack of adequate data, a meaningful correlation of the effect of speed on NO_x emissions is not possible. Consequently, the same procedure was used for correlating NO_x emissions as was used for the carbon monoxide emissions. The data in Figs. 20 and 21 include a wide range of engine variables and, in spite of this variation of conditions, fall into a fairly well-defined band. These data then indicate the levels of NO_x emissions expected in a normally operated engine.

For direct injection engines,

$$\begin{aligned} \text{NO}_x &= 23.40 + 1.488 \times 10^4 (\text{FA}) + 1.319 \times 10^6 (\text{FA})^2 \\ &\quad - 1.490 \times 10^8 (\text{FA})^3 \end{aligned} \quad [\text{Eq. 3.16}]$$

For precombustion chamber engines,

$$\begin{aligned} \text{NO}_x &= -6.566 + 2.530 \times 10^4 (\text{FA}) - 2.51 \times 10^4 (\text{FA})^2 \\ &\quad - 5.01 \times 10^6 (\text{FA})^3 \end{aligned} \quad [\text{Eq. 3.17}]$$

where

NO_x = parts per million NO_x on a dry volume basis

FA = fuel-air ratio--lb/lb

As discussed previously, the fuel-air ratio correlates well with indicated mean effective pressure. Thus, the NO_x emissions can also be correlated directly with engine output, as given by the following relations:

$$\text{IMEP}_C = \text{IMEP}(p_{i,nt}/29.92)^{-0.747} \quad [\text{Eq. 3.13}]$$

For direct injection engines,

$$\begin{aligned} \text{NO}_x &= 61.56 + 5.066(\text{IMEP}_C) - 0.01529(\text{IMEP}_C)^2 \\ &\quad + 1.66 \times 10^{-3}(\text{IMEP}_C)^3 - 7.354 \times 10^{-6}(\text{IMEP}_C)^4 \end{aligned} \quad [\text{Eq. 3.18}]$$

For precombustion chamber engines,

$$\begin{aligned} \text{NO}_x &= 72.50 + 1.2614(\text{IMEP}_c) + 1.080(\text{IMEP}_c)^2 \\ &\quad - 6.617 \times 10^{-4}(\text{IMEP}_c)^3 \end{aligned} \quad [\text{Eq. 3.19}]$$

where

NO_x = parts per million NO_x on a dry volume basis

IMEP_c = corrected engine indicated mean effective pressure--psi

IMEP = actual engine indicated mean effective pressure

P_{int} = intake manifold pressure--inches of mercury absolute

These results are shown in Figs. 24 and 25 for various intake manifold pressures.

Since the concentration of NO_x tends to increase with the power output of a CI engine, it is also expected that the total emission rate of pollutants is related to the power output of an engine. This is borne out by the data in Fig. 26 which show the emission rate of NO_x (calculated as NO_2) in pounds per hour plotted as a function of engine brake horsepower for various precombustion chamber and direct injection engines from 10 to 3,000 horsepower. The line drawn through the data corresponds to the condition in which the mass emission rate of NO_x is a linear function of brake horsepower. Although individual engines may vary somewhat from direct proportionality, overall the trend is quite close to being linear. Thus, Fig. 26 provides a rapid estimate of the rate of NO_x emissions, strictly from the load requirements of an engine.

Hydrocarbon Emissions

Attempts at correlation of hydrocarbon emissions for CI engines were not successful. Hydrocarbons are among the most difficult of CI engine emissions to measure and some of the difficulty in correlations may be due to large errors in experimental measurements. The hydrocarbons formed in a CI engine are due to incomplete mixing and combustion and are, therefore, dependent on individual combustion chamber and injector design and engine condition. Also adding to the difficulties is the problem encountered with other emissions from CI engines, that of lack of complete engine data with which to attempt a correlation. In most cases in the literature, little more than fuel-air ratio is available for correlation purposes.

Figure 27 shows hydrocarbon emissions from many CI engines as a function of fuel-air ratio. A wide range of emissions levels was observed as well as different qualitative behavior. Some engines showed hydrocarbon emissions decreasing with increasing fuel-air ratio, while others showed increased hydrocarbon emissions with increasing fuel-air ratio. Intermediate behavior was also observed in which hydrocarbons showed varying trends with fuel-air ratios or essentially no effect. Similar inconsistent behavior was observed in the

few instances where effects of other variables such as spark timing and engine speed were studied.

In an effort to obtain some meaningful summary of the hydrocarbon emission data, a plot of frequency of observed hydrocarbon emission as a function of emission level was made for the available data. The results shown in Fig. 28 indicate that the majority of the observed hydrocarbon emissions data points fall in the range of 0 to 300 parts per million carbon. (Using the measure common in automobile emissions, this is equivalent to the range of 0 to 50 parts per million equivalent hexane.) Although this type of correlation is far from precise, it does give an indication of the levels of hydrocarbon emissions expected in engine operation.

Smoke

A survey of the literature concerning smoke emissions from compression ignition engines showed that an attempt to correlate smoke with engine parameters would be ill-advised. Smoke is very dependent on nozzle and combustion chamber design which immediately presents severe limitations to correlation attempts. Fuel variables are also very important in determining smoke levels. These variables include basic fuel composition and volatility along with the nature and amount of fuel additives. A further difficulty is correlation of smokemeter readings. After much study, there is still some disagreement as to the relation between the readings obtained from the various techniques of measuring smoke.

Since the correlation of smoke with engine parameters does not appear feasible, the approach taken was that of obtaining approximate correlation between the various types of smokemeters. The reason for this approach is to be able to make reasonable corrections of various reported smoke values or experimental measurements to some common standard. These types of meters are listed below, with examples of each.

Light Extinction
Hartridge
Public Health
CRC

Spot Filter
Bosch
Bachrach

Visual Rating
Ringlemann

Moving Strip Filter
Von Brand

Figures 29 through 34 show correlations that have been reported recently in the literature concerning the various smokemeters. In the cases where more than one correlation is presented, it is not possible, based on current knowledge, to determine which, if any, of the correlations is correct. Consequently, an average value for the correlation should probably be used.

PART IV: GAS TURBINE EMISSIONS

Emissions data from gas turbines have been in very short supply. Only recently has a substantial amount of data become available. In order to obtain the largest possible amount of data, the results in this section include data from turbojet aircraft engines. The emissions data from these engines are similar to those from conventional gas turbines. This is to be expected since the combustion process is basically the same in both types of power plants. Gas turbine emission data usually are accompanied by little more than overall fuel-air ratio, if that. Consequently, it is essentially the only operating variable with which one can hope to correlate emission data. In gas turbines the burner operates at richer fuel-air mixtures than the overall fuel-air ratio and the combustion gases in the burner are then diluted with air to control turbine inlet temperature. The fuel-air ratio in the burner, therefore, would be expected to be more significant than the overall fuel-air ratio in determining emissions characteristics. Other variables of interest would be the burner temperatures and residence times. Such data, unfortunately, are rarely available, and correlation attempts are restricted to overall fuel-air ratio.

The results of some attempts at correlation with overall fuel-air ratio are given in Figs. 35, 36, and 37. The data in these figures were obtained from the gas turbine emission references in Bibliography. These figures show emissions index (EI) as a function of overall fuel air equivalence ratio for carbon monoxide, oxides of nitrogen, and hydrocarbons. The emissions index gives emissions data in terms of pounds of pollutant per 1000 pounds of fuel consumed. It can be calculated by the following relations:

$$EI = \frac{M_i}{M_e} \left[\frac{1}{FA} + 1 \right] \left[\frac{\text{ppm}}{10^3} \right] \quad [\text{Eq. 4.1}]$$

where

M_i = molecular weight of species of interest

M_e = molecular weight of exhaust gas

FA = fuel-air ratio--lb/lb

ppm = concentration of species of interest in parts per million
by volume

As would be expected from the previous discussion, there is no discernible correlation between emissions and overall fuel-air ratio. Since the emissions do not correlate well with the only available variable, fuel-air ratio, the same procedure was used as in the case of compression ignition engine hydrocarbon emissions. Figure 38 shows a plot of frequency of observed emission indices for turbine type engines. It can be seen that a typical gas turbine would emit between 0 and 10 pounds of CO; 0 and 3 pounds of NO_x; and 0 and 1 pound of hydrocarbons per 1000 pounds of fuel consumed.

PART V: SMALL HEATING PLANT FURNACES

The analysis of potential air pollution problems involving small- to medium-sized heating plants has been handicapped by the lack of consistent and accurate information on the composition of the exhaust gases being emitted under the specific operating conditions. The overall objective of Part V is to examine the feasibility of developing models for predicting the constituents of exhaust gases from small- to medium-sized heating plant furnaces under various load conditions and using various fuels. The pollutants to be examined are oxides of nitrogen, total hydrocarbons, carbon monoxide, carbon dioxide, sulfur dioxide, sulfur trioxide, and particulates.

The classification as to the size of heating plants varies, depending on fuel. For combustion sources using coal, the breakdown for various units is as follows (Ref. 22): Units having energy inputs greater than 10^8 Btu per hour are classified in the power plant category; units having an input in the range of 10^7 to 10^8 Btu per hour are classified as industrial; units having less than 10^7 Btu per hour input are classified as domestic-commercial installations. Combustion sources, which include power plant installations, are units which have heating units delivering over 1,000 Hp, whereas small sources, which include both industrial and commercial-domestic sources, have heating units delivering less than 1,000 Hp. In order to standardize the classification as to the size of a heating plant, the Hp rating for oil units will be converted to a Btu/hr rating. The basis for converting from Hp to Btu per hour for oil-fired units in this section assumes an average heating value of 18,300 Btu per pound of oil and the equivalence $1,000 \text{ Hp} = 2,500$ pounds of oil per hour (Ref. 23). This equivalence assumes a 75 percent energy conversion efficiency. From this, it is seen that, for oil, an energy input greater than 4.6×10^6 Btu per hour is considered a large source, whereas units with less than this are considered small; i.e., industrial or commercial-domestic. For the report that follows, all installations having an energy input below 10^7 Btu/hr will be assumed to be either industrial or commercial-domestic.

For commercial-domestic installations, the most commonly used fuels are oil and gas, whereas, for small industrial boilers, coal is also used. In that oil and gas are the most often used fuels in the heating plants of interest in the present study, a description of these fuels is appropriate. In particular, fuel oil classifications warrant further attention. The classification of fuel oils used in small installations is kerosene, diesel fuel, and grades one through six oils. The most common oil fuel use pattern is grade 2 in domestic units, grade 4 in units up to 10^6 Btu per hour, grades 4 through 6 in units up to 10^7 Btu per hour, and grade 6 for residual oils in units above 10^7 Btu per hour. Kerosene and diesel oil are used in units smaller than 10^6 Btu per hour (Ref. 22).

It should be recognized at the outset that the data exhibit a great variability due to furnace types, furnace conditions, fuels, and unreliable measuring techniques. A certain caution must, therefore, be exercised in using any of the equations to predict the behavior of any particular source. The calculated value represents only some average condition. Variabilities exceeding 100 percent can be expected for some operating conditions.

Particulates

The emission profile of a given coal-burning furnace is related to many factors (Ref. 22): gas velocity, particle size, particle density, fuel burning rate, combustion efficiency, fuel gas temperature, furnace configuration, coal composition and size, and the initial state of the raw coal. The effect of the above variables on the particulate emission rate is shown in the table below.

<u>Variable Increasing</u>	<u>Mass Particulate Rate†</u>
Gas velocity	I
Particle size	D
Particle density	D
Coal ash	I
Coal size	D
Coal fired in suspension	I
Coal burning rate	I
Coal heat value	D
Combustion efficiency	D
Boiler efficiency	D

The variables which are considered to be most important in relation to particulate emissions from coal-fired furnaces include (Ref. 22)

- (1) the amount of ash in the coal,
- (2) the heat content or heating value of the coal,
- (3) the method of burning the coal, and
- (4) the rate at which the coal is burned.

The primary variable for correlating stack emissions to fuel composition is the heat content of the fuel.

Figure 39 presents a nomograph which accounts for these variables in predicting the average particulate emissions to be expected from utility- and industrial-sized boilers without control equipment. Because the use of coal in commercial-domestic size installations is in a rapid state of decline, emissions

†"I" denotes increase; "D" denotes decrease.

on these installations are not discussed. The preferred fuels for commercial-type domestic boilers are gas and oil.

Smoke from oil-burning units is the result of an inefficiently operated furnace. Incomplete atomization caused by improper fuel temperature, dirty, worn, or damaged burner tips, or improper fuel or steam pressure may cause the furnace to smoke. Other factors affecting emission rates include improper fuel-to-air ratio, poor mixing of the air and oil mixture, low furnace temperatures, and insufficient time for the fuel to burn completely in the combustion chamber. Because of the multi-variable nature of the system under consideration and the limited amount of data available, an analytical predictor equation for smoke emissions from oil-fired units was not attempted. Rather, a frequency distribution of particulates from oil-fired small sources is given in Fig. 40. As can be seen from the figure, the particulate emissions for small sources vary from 0 to 10 pounds of particulates per 1,000 pounds of oil fired, with 79 percent of the emissions lying between 1 and 4 pounds per 1,000 of oil fired. The most probable emission rates fell between 1 and 2 pounds of particulates per pound of oil fired with 42 percent of the values reported being in this range. The effect of pertinent variables on particulate emission rates from oil-fired burners is shown below.

<u>Variable Increasing</u>	<u>Mass Particulate Rate†</u>
Percent load	--
Fuel temperature	D
Fuel pressure	D
Excess air	I
Percent CO ₂ in stack	I
Dirt in firebox	I
Flue gas recirculation	I
Flame temperature	D
Stack temperature	D
Percent sulfur in oil	I
Percent ash in oil	I

The emission rates of particulates from gas-fired installations are negligible.

†"I" denotes increase; "D" denotes decrease; "--" denotes no change.

Carbon Dioxide

It is frequently necessary to calculate the theoretical air requirements for burning a fuel and the products of combustion associated with the process. The equations that are given below are particularly useful for calculating the expected CO_2 emissions for gas, liquid, and solid fuels under ideal conditions (stoichiometric conditions). Standard conditions for these calculations are 60°F and 29.92 inches mercury for the temperature and pressure, respectively.

The air required for perfect combustion of one cubic foot of any gaseous fuel is (Ref. 24). In generating Eq. (5.1), it has been assumed that air is composed of 0.232 lbs of oxygen per pound of air.

$$\begin{aligned} \frac{\text{cu ft air}}{\text{cu ft fuel}} = & (\% \text{ CH}_4 \times 0.0956) + (\% \text{ C}_2\text{H}_6 \times 0.1675) \\ & + (\% \text{ C}_3\text{H}_8 \times 0.239) + (\% \text{ C}_4\text{H}_{10} \times 0.311) \\ & + (\% \text{ H}_2 \times 0.0239) + (\% \text{ CO} \times 0.0239) \\ & - (\% \text{ O}_2 \times 0.0478) \end{aligned} \quad [\text{Eq. 5.1}]$$

where all the percentages are by percents by volume from the volumetric analysis of the fuel to be burned. It should be noted that the gas and air volumes in the above equation must be measured at the same temperature and pressure. If corrections are to be made, the following equations are useful.

$$\text{Volume at } T_2 = \text{volume at } T_1 \times \frac{T_1 + 460}{T_2 + 460} \quad [\text{Eq. 5.2}]$$

$$\text{Volume at } P_2 = \text{volume at } P_1 \times \frac{P_1}{P_2} \quad [\text{Eq. 5.3}]$$

For liquid and solid fuels, the theoretical air/fuel ratio is (Ref. 24)

$$\begin{aligned} \frac{\text{cu ft air}}{\text{lb fuel}} = & (\% \text{ C} \times 1.514) + (\% \text{ H} \times 4.54) + (\% \text{ S} \times 0.568) \\ & - (\% \text{ O} \times 0.568) \end{aligned} \quad [\text{Eq. 5.4}]$$

where all the percentages are percents by weight from the ultimate analysis of the fuel to be burned. Note that the cubic foot of air in the above equation is measured at 60°F and 29.92 inches of mercury.

To predict the theoretical quantity of CO_2 in the products of combustion, the following equations are used. For gaseous fuels, one uses (Ref. 24)

$$\begin{aligned} \frac{\text{lb CO}_2}{\text{cu ft fuel}} = & (\% \text{ CO} \times 0.001165) + (\% \text{ CH}_4 \times 0.001165) \\ & + (\% \text{ C}_2\text{H}_6 \times 0.00230) + (\% \text{ C}_3\text{H}_8 \times 0.00349) \\ & + (\% \text{ C}_4\text{H}_{10} \times 0.00465) + (\% \text{ CO}_2 \times 0.001164) \end{aligned} \quad [\text{Eq. 5.5}]$$

All percentages in the above equation are percents by volume of the constituents in the volumetric analysis of the fuel. For liquid and solid fuels, the following equation is used (Ref. 24).

$$\frac{\text{lb CO}_2}{\text{lb fuel}} = (\% \text{ C} \times 0.0367) + (\% \text{ CO}_2 \times 0.01) \quad [\text{Eq. 5.6}]$$

All percentages in the above equation are percents by weight of the constituents in the ultimate analysis of the fuel.

If the percent C includes the unavailable carbon already in the form of CO_2 , the last term is omitted.

The predictor equations for CO_2 based on mass in this section give the upper limit of emissions to be expected from gaseous, liquid, and solid fuels.

Carbon Monoxide Emissions

The normal range, i.e., the most probable range, of emissions of carbon monoxide from small oil-fired boilers is between 0 and 1 pound carbon monoxide per 1,000 pounds of oil (Ref. 23). Emission factors for coal-fired installations include 0.02 pound per million Btu for power plants, 0.1 pound per million Btu for industrial stokers, and 2 pounds per million Btu for domestic units (Ref. 21). Very little reliable data are available in the literature concerning carbon monoxide emissions.

Sulfur Oxides

The amount of sulfur emitted as sulfur dioxide may be inferred from a material balance. The sulfur content in coal ranges from 1 percent to greater than 10 percent by weight. During the combustion of coal, sulfur dioxide, sulfur trioxide, and some fly ash-sulfur oxide complexes are formed. In addition, for very inefficient combustion, hydrogen sulfide may also be evolved. A material balance on a coal system reveals that, on the average, 2 percent of the sulfur goes into the slag or residue and 1 to 2 percent goes into SO_3 (Ref. 22). In the event that no appreciable H_2S is formed, 95 percent of the sulfur in the coal is emitted to the atmosphere as SO_2 (Ref. 22). Based on this information, the emission rates of SO_2 from coal-fired furnaces can be calculated by

$$\frac{\text{lb SO}_2}{1,000 \text{ lb fuel}} = 0.95(0.02 \times \% \text{ S}) \times 10^3 \quad [\text{Eq. 5.7}]$$

where the percent sulfur is by weight.

The oil used in oil-fired units contains complex organic forms of sulfur which vary in amount between 0 and 5 percent by weight (Ref. 23). During combustion, sulfur in the oil is oxidized to SO_2 , SO_3 , and sulfate radicals. A material balance on the emissions from oil-fired furnaces reveals that, on the average, 98 percent of the sulfur is emitted as SO_2 , 1 percent as SO_3 , and 1 percent complexed with the fly ash (Ref. 23). Based on this, the emission rates of SO_2 from oil-fired furnaces can be calculated by

$$\frac{\text{lb SO}_2}{1,000 \text{ lb fuel}} = 0.98(0.02 \times \% \text{ S}) \times 10^3 \quad [\text{Eq. 5.8}]$$

where the percent sulfur is by weight. The range of SO_2 values reported in the literature is shown in Fig. 41. The emission rates of SO_2 from gas-fired installations are negligible.

The emission rates of sulfur to trioxide to the atmosphere are not a direct function of the percent sulfur in coal or oil as in the case for SO_2 . The degree of scatter can be seen in Fig. 42. The significance of SO_3 formation lies in the fact that, when the stack gases are cooled below the dew point, much of the SO_3 combines with water vapor to either deposit on some surface as H_2SO_4 or produce a visible plume. The effect of flame temperature on SO_3 emissions is shown in Fig. 43. Other factors which have effects on SO_3 emissions from oil-fired units are given below.

<u>Increasing Operating Variables</u>	<u>SO_3 †</u>
Percent load	I
Fuel temperature	I
Fuel pressure	I
Excess air	I
Percent CO in stack	D
Dirt in firebox	I
Flue gas recirculation	--
Flame temperature	I
Stack temperature	I
Percent sulfur in oil	I
Percent ash in oil	D

The most likely occurrence of H_2S is expected to be found in hand-fired (coal) stoves. The average value reported for hand-fired units is 0.4 percent of sulfur in the coal (Ref. 26).

Oxides of Nitrogen

Oxides of nitrogen are produced when fossil fuel combustion takes place using air as an oxidant. At adiabatic flame temperatures, the combination of

†"I" denotes increase; "D" denotes decrease; "--" denotes no change.

atmospheric oxygen and nitrogen results in the formation of nitric oxide, NO. As shown in Fig. 44, NO formation for methane-air combustion at atmospheric pressures is favored at only high temperature. NO, however, remains a "pseudo-stable" species even at low temperatures because of kinetic limitations of its rate of decomposition. The relationship between equilibrium NO_x concentrations and the corresponding adiabatic flame temperatures is shown in Fig. 44. For methane, it should be noted that the maximum equilibrium concentration of NO_x occurs when the air/fuel ratio is approximately 1.15. In contrast, the maximum flame temperature is reached at conditions below the stoichiometric ratio. The equilibrium amounts of NO and NO₂ as a function of temperature are shown in Fig. 45. For most stationary combustion processes, the residence time available is too short for the oxidation of nitric oxide to nitrogen dioxide, the thermodynamically favored species at lower temperatures. Thus, although NO_x emissions are usually expressed as "equivalent NO₂," the combustion gases are predominantly in the form of NO.

Based on experimental evidence, another source of nitrogen for oxide formation is the organically bound nitrogen in the fuel. Nitrogen-containing fuels, such as coal or fuel oil, can produce NO₂, NO, and, possibly, N₂, depending on the reducing nature of the flame. The role of fuel nitrogen appears to vary from being dominant at low temperatures and being negligible at high temperatures; i.e., near equilibrium conditions.

Based on the above, it is clear that factors affecting NO_x emissions from fossil fuel combustion processes are more complex than the understanding of the nitrogen-oxygen fixation process as a function of chemical thermodynamic and kinetic considerations. Further, it is known that chemically bound nitrogen in the fuel, either coal or oil, is oxidized more readily to NO_x than highly stable molecular carbon is oxidized to CO₂ or CO and, consequently, the organically bound nitrogen plays a role in NO_x formation. In general, the major factors influencing NO_x emissions from combustion sources, in addition to the flame temperature, include

- (1) excess air,
- (2) heat release and mixing,
- (3) mass transport and mixing, and
- (4) fuel type and composition.

The reduction of the excess air reduces the NO_x emissions, whereas high heat release rates lead to increased NO_x emissions. The dependency of NO emissions on excess air is shown in Fig. 46. The reason for the increased NO_x emissions with high heat release rates lies in the extreme sensitivity of NO_x formation equilibrium and kinetics to peak temperatures. The distribution of fuel and air in the combustion chamber can also materially affect NO_x emissions. Practices which include internal recirculation or back-mixing of combustion gases dilute the primary flame zone, thus reducing its temperature and the NO_x formation rates. The fuel type affects NO_x formation through two mechanisms: the theoretically attainable flame temperatures and the rate of radiative heat transfer. The "rule of thumb" for ranking NO_x-forming tendencies of fuel for small to intermediate boilers is coal, oil, and gas in descending order. With regard to fuel composition, the role of chemically bound nitrogen in NO_x formation is definitely established. The extent of the contribution of nitrogen

in the fuel to the total NO_x emissions varies with the temperature level of the combustion process from being all important at low temperatures to being negligible near equilibrium.

The comparison of emissions for coal, oil, and gas, or equivalent basis, is given for commercial-domestic, industry, and utilities in Table 1.

TABLE 1
COMPARISON OF COAL, OIL, AND GAS
ON EQUIVALENT BTU BASIS (REF. 29)

Fuel	Average NO_x Emissions in Boilers and Power Plants ($\text{lb NO}_x / 10^9 \text{ Btu}$)		
	Household and Commercial	Industry	Electric Power Generation
1. Natural Gas (1,046 Btu/cu ft) (30)	111	205	373
2. Fuel Oil (149,966 Btu/gal) (30)	80-480	480	693
3. Coal (11,867 Btu/lb) (30)	337	842	842

Because NO_x emissions depend in great measure on such variables as installation size, type of barrier, cooling surface area, firing rate, and the air/fuel ratio, the determination of accurate predictor equations is very difficult. The degree of difficulty can better be appreciated by examining the following quotation taken from Report No. 3 of the Joint Los Angeles County Report (Ref. 28):

"In the determination of an NO_x emission factor for power plants, some 130 tests including 554 individual samples were considered. The Department of Water and Power of the City of Los Angeles has been making an extensive study of the effect of operating variables on NO_x emissions. These studies have included a testing program in which two to three tests per week were performed for a period greater than a year.

The rates of emission of NO_x from units as complex as these, with the possibility of a number of constantly fluctuating operating variables, may be assumed to be constantly fluctuating also. In these circumstances, the rate of emission of NO_x at any given instant in any plant may be different from the rate of emission at the next instant. Experience gained during the carrying out of the project has shown these assumptions to be true. A striking example of this variability is the fact that samples taken as nearly at the same time as possible from two probes in as close proximity to each other as possible

show two different values for NO_x concentrations. It was found that actual rates of NO_x emission from sister units may be different for operating conditions which are the same for each unit within the limits of ability to determine. This phenomenon has been verified repeatedly.

Thus, it may be seen that in the development of an emission factor, calculations must be based on averages of many data taken from many different conditions. As pointed out in the discussion of asphalt paving plants, the use of such a factor to determine the rate of NO_x emission from a single unit at any given time may produce data which are far from reliable for the conditions existing at that time.

During the carrying out of the test program on power plant boilers, a number of phenomena were brought to light. Instead of clarifying the situation, many of these observations served merely to point up the complexity of the problems. It should be borne in mind that the examples and curves shown are in each case for some particular unit and should not be construed to be correction factors for measured emission rates from any other unit. The degree and direction of the effect of operating variables upon NO_x production must be determined individually for each particular unit to be considered."

What can be attempted in light of the above, with a limited degree of success, is the generation of equations which represent average or typical emissions from various installations. Figure 47 gives the NO_x emissions from gas-fired refinery furnaces. It is expected that these emissions are indicative of most gas-fired process heaters. The average emissions can be estimated using the following equation,

$$\text{LOG}(\text{NO}_x) = 1.14 \text{ LOG}(\text{HI}) - 8.1 \quad [\text{Eq. 5.9}]$$

where $\text{LOG}(\text{NO}_x)$ is the common logarithm of the emission rate, in lb/hr, and $\text{LOG}(\text{HI})$ is the common logarithm of the firing rate in Btu/hr. Figure 48 depicts a composite relationship for coal, oil, and gas, giving NO_x emissions versus the gross heat input. An equation relating the average emission rates, in lb/hr, for coal, oil, and gas to the gross heating input is given below.

$$\text{LOG}(\text{NO}_x) = \text{LOG}(\text{HI}) - 6.85 \quad [\text{Eq. 5.10}]$$

where $\text{LOG}(\text{NO}_x)$ is the common logarithm of the emission rate, in lb/hr, and $\text{LOG}(\text{HI})$ is the common logarithm of the gross heating input in Btu/hr.

Table 2 gives common emission factors for nitrogen oxides emissions from household-commercial, industry, and utilities using coal, oil, and gas as fuels.

Hydrocarbons

The polynuclear hydrocarbons emissions obtained from coal-burning units vary widely, depending on the quality of combustion achieved. Emissions from oil-burning sources were generally much lower than from coal-burning sources of equivalent size. Gas-burning emission rates were the lowest in hydrocarbons of all fuel sources. Hydrocarbon emissions from gas-burning units are assumed to be negligible.

TABLE 2
EMISSION FACTORS FOR NITROGEN OXIDES (REF. 27)

Source	Average Emission Factor
Coal	
Household and Commercial	8 lb/ton of coal burned
Industry	20 lb/ton of coal burned
Utility	20 lb/ton of coal burned
Fuel Oil	
Household and Commercial	12-72 lb/1000 gal of oil burned
Industry	72 lb/1000 gal of oil burned
Utility	104 lb/1000 gal of oil burned
Natural Gas	
Household and Commercial	116 lb/million c.f. of gas burned
Industry	214 lb/million c.f. of gas burned
Utility	390 lb/million c.f. of gas burned

Because of the limited amount of data available in the literature, a meaningful predictor for total hydrocarbons could not be generated. The trend and orders of magnitudes of emissions from small sources burning oil and coal can be deduced from Fig. 49.

Effect of Operating Variables on Oil-Fired Furnaces

The discussion in this section will center around the performance characteristics obtained under controlled conditions for high pressure atomizing gun burners which are used in domestic oil-fired furnaces. The laboratory results to be presented will include smoke, carbon monoxide, total hydrocarbons, and nitrogen oxides emissions measured over the entire range of air-fuel ratios for several burner configurations. The basic reference for this section is a paper by Howekamp and Hooper (Ref. 31).

Smoke Emissions

In all smoke emission tests, a modified sequential tape sampler was operated to determine smoke levels. The resultant spots on the sampler were measured on a reflectance photometer and then converted to Shell-Bachrach index units.

Figure 50 demonstrates an interesting effect resulting from varying the on-off periods of the cycle. With an excess air setting of 20 percent, runs were made with preceding off-periods of 10, 15, 20, and 30 minutes. The results shown in Fig. 44 show a near linear decrease in smoke with time during on-periods.

Figure 51 shows average smoke emissions vs. air/fuel ratio for various types of fuel nozzle and air-fuel mixing assemblies, while Fig. 52 shows the

emissions during the tenth minute of the on-period. The average numbers suggest that the meaningful air pollution measurement is not the one taken during hot running conditions. Further, the levels shown in Fig. 46 are considerably lower during the tenth minute of operation than during start-up as would be expected.

Gaseous Emissions

Automatic analyzers and recorders were used to monitor O_2 , CO_2 , CO, and gaseous hydrocarbons (methane). Integrated flue gas samples were collected and analyzed for oxides of nitrogen by the phenodisulfonic acid method.

Emissions of CO and gaseous hydrocarbons are shown in Figs. 53 and 54. Although the shapes of the curves are similar, the carbon monoxide emissions were considerably greater than the hydrocarbon emissions.

The striking feature of all the above results is the degree of emission control one can realize from a judicious choice of operating air-fuel ratio for all the pollutants, except oxides of nitrogen. The data suggest that air-fuel ratios ranging from 1.8 to 2.0 virtually eliminate smoke, CO, and hydrocarbon emissions. Unfortunately, incompatibilities exist with regard to the control of NO_x and the remaining gaseous pollutants. Figure 55 shows that the condition which minimizes CO, hydrocarbons, and smoke maximizes the generation of NO. Likewise, the condition which minimizes NO emissions is undesirable for controlling the other gaseous pollutants.

Finally, it should be noted that the optimum running condition for controlling emissions reduced the efficiency of operation in all cases tested. This effect is shown in Fig. 56.

PART VI: CONCLUSIONS

1. Spark Ignition Engines. Emissions of carbon monoxide and oxides of nitrogen can be predicted by use of common engine operating parameters. For carbon monoxide the air-fuel ratio to the engine is sufficient, while oxides of nitrogen predictions can be made using the air-fuel ratio, spark timing and intake manifold pressure. The levels of hydrocarbon emissions from spark ignition engines cannot be readily predicted. The trends of variables such as air-fuel ratio, spark timing, compression ratio can be approximated but the absolute level of hydrocarbon emissions appears to be dependent on the specific engine in question. Pre-combustion chamber compression ignition engines have oxide of nitrogen emissions levels approximately one-half those of direct injection engines.
2. Compression Ignition Engines. Emissions of carbon monoxide and oxides of nitrogen can be predicted by use of the engine fuel-air ratio. Since the indicated mean effective pressure of compression ignition engines correlates well with fuel-air ratio, emissions of carbon monoxide and oxides of nitrogen can also be predicted by use of engine output in terms of indicated mean effective pressure. Hydrocarbon emission levels vary widely from engine to engine and a prediction of these levels is restricted to an average emission level for a typical compression ignition engine. Prediction of the level of smoke emissions is not feasible.
3. Gas Turbines. Prediction of emissions from gas turbines is restricted to average emission levels for a typical gas turbine. A severe problem encountered in attempts to correlate gas turbine emissions is a lack of published data on turbine parameters.
4. Average particulate emission to be expected from a typical coal burning installation can be predicted. Emissions for any one particular furnace, however, cannot be estimated with any degree of accuracy. A quantitative estimate of the effect of operating variables on particulate emission from coal or oil burning furnace is not possible.
5. Carbon monoxide emissions from fossil fuel burning installations are insignificant if proper firing conditions are maintained.
6. The amount of sulfur oxides emitted to the atmosphere is completely dependent on the amount of sulfur contained in the fuel. A knowledge of the ultimate analysis of the fuel being burned will allow an accurate prediction of the amount of SO_2 being emitted to the atmosphere.

7. Average oxides of nitrogen emission to be expected from a typical fossil fuel burning installation can be predicted. Emissions from a particular furnace cannot be estimated with any degree of accuracy. A quantitative estimate of the effect of operating variables on oxides of nitrogen emission is not possible at present.
8. Hydrocarbon emissions from fossil fuel burning installations cannot be predicted.

PART VII: RECOMMENDATIONS

In order to obtain more data on which to base emissions correlations, further research should be carried out in the following areas:

1. Hydrocarbon emissions from spark ignition and compression-ignition engines. More work is needed in order to determine quantitatively how significant engine variables determine the level of hydrocarbon emissions from these engines.
2. Total emissions from gas turbines. More emissions work should be performed on gas turbines in which all the relevant variables are measured. Most gas turbine emissions studies in the literature present little more than overall fuel air ratio of the turbine. The results of this study show that this parameter is not sufficient to predict gas turbine emissions.
3. Oxide of nitrogen emission from fossil fuel burning installations. A study is needed to quantify the effect of operating variables on the emissions of nitrogen oxides. This is particularly important for commercial-domestic size units which make up a large fraction of the units used in military bases.
4. Hydrocarbon emissions from fossil fuel burning installations. A study to define the type and magnitude of hydrocarbon emission is needed. The study will allow an estimate of the magnitude of the problem.
5. Optimization of operating condition for minimum emissions for commercial-domestic units.

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* indicates information on atmospheric emissions from coal combustion

† indicates information on atmospheric emissions from fuel oil combustion

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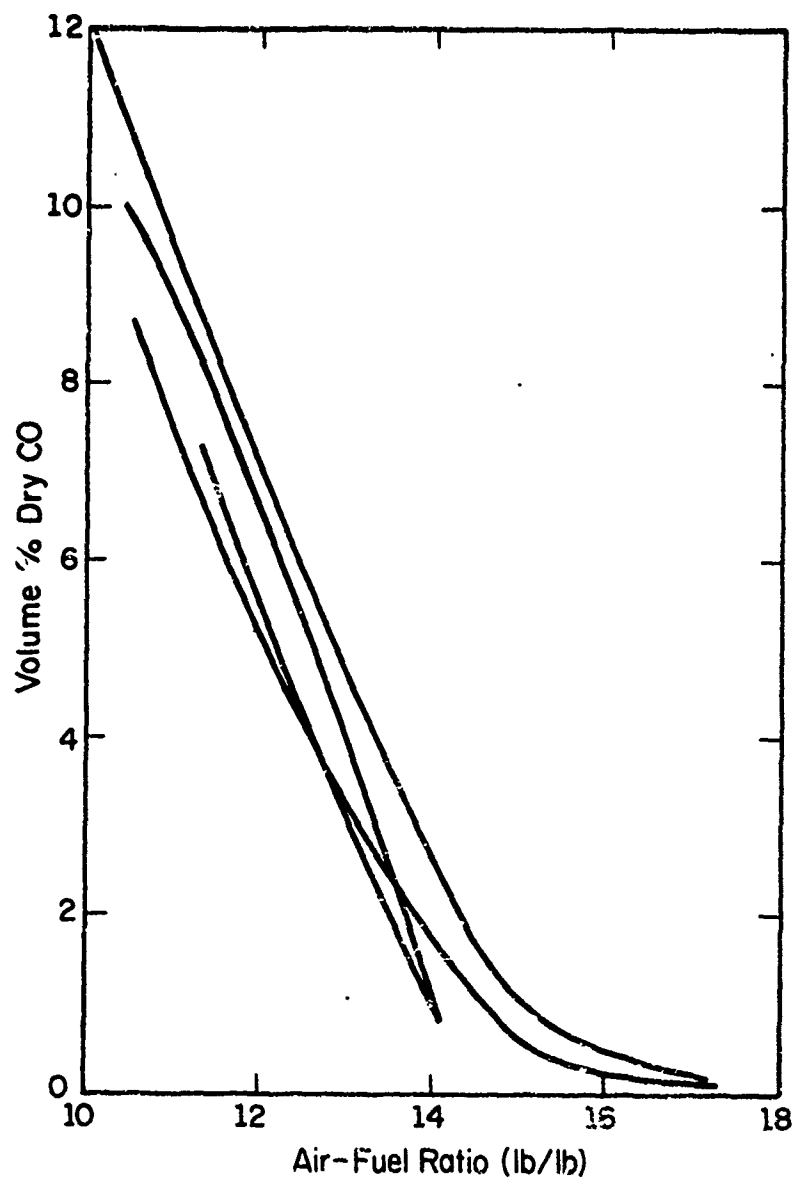


Figure 1 Experimental Carbon Monoxide Concentration vs. Air Fuel Ratio--Spark Ignition Engine

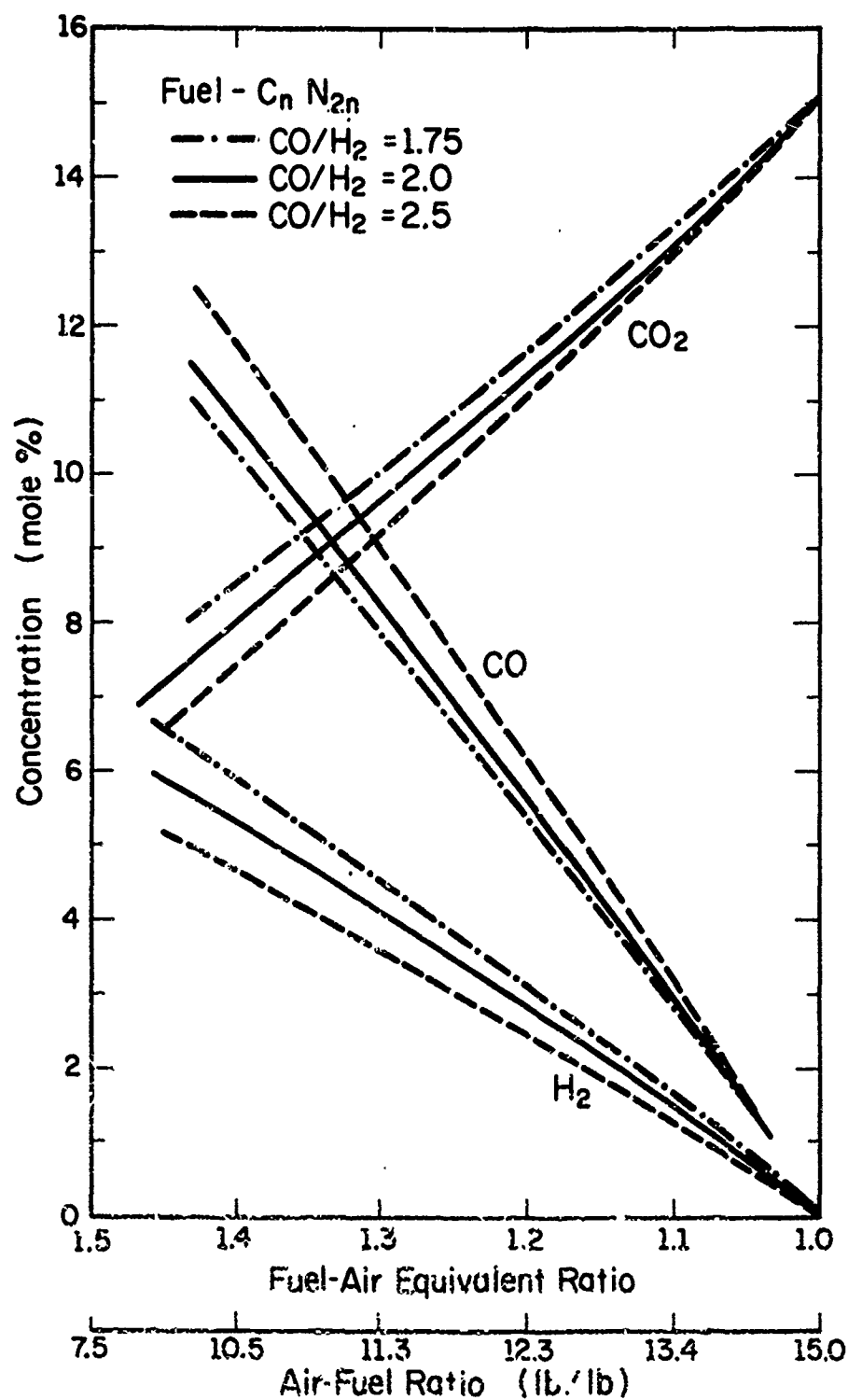


Figure 2 Predicted Carbon Monoxide, Carbon Dioxide, and Hydrogen Concentration vs. Fuel Air Equivalence Ratio--Spark Ignition Engine

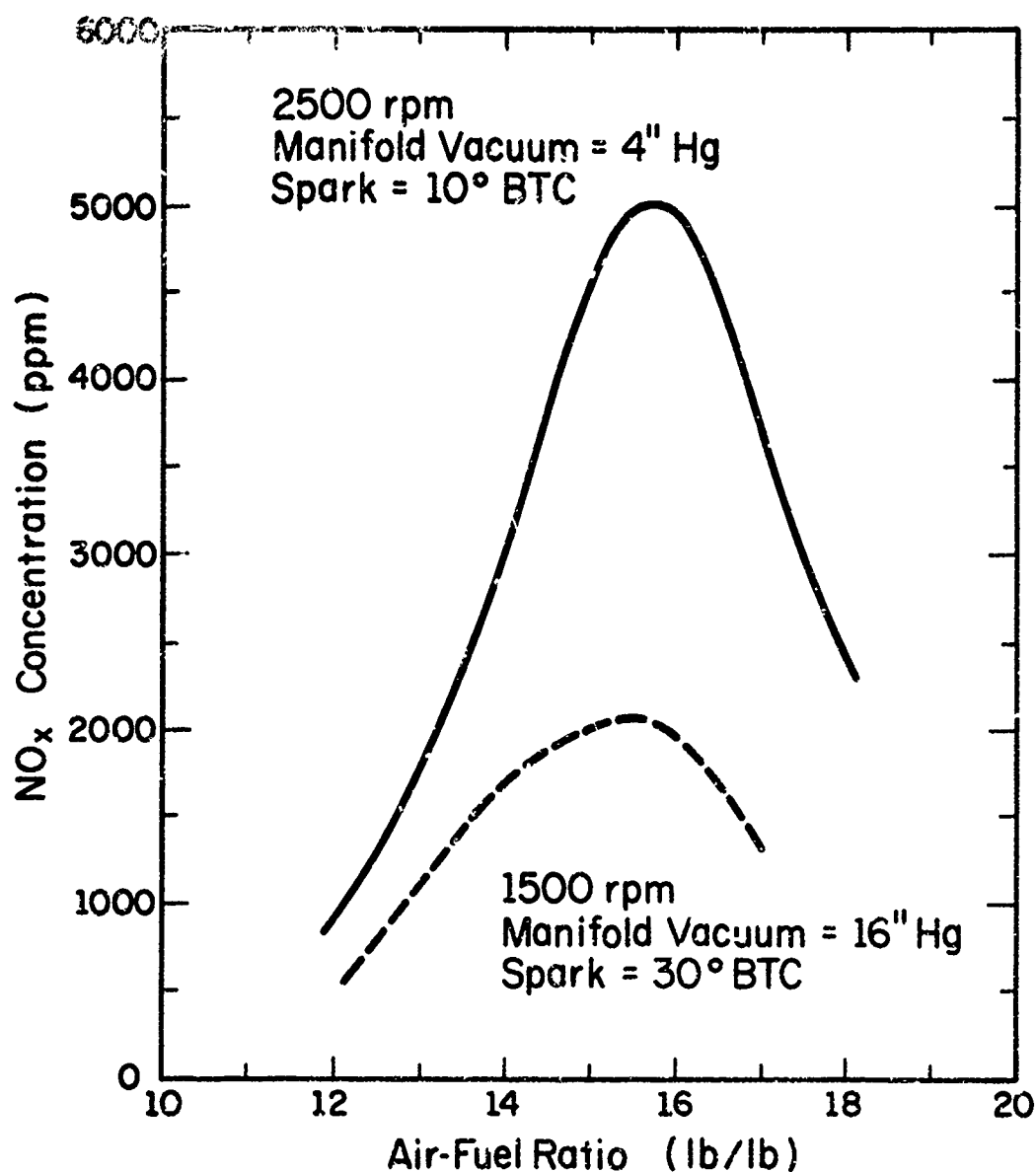


Figure 3 Typical Experimental Oxides of Nitrogen Concentration as a Function of Spark Ignition Engine Variables

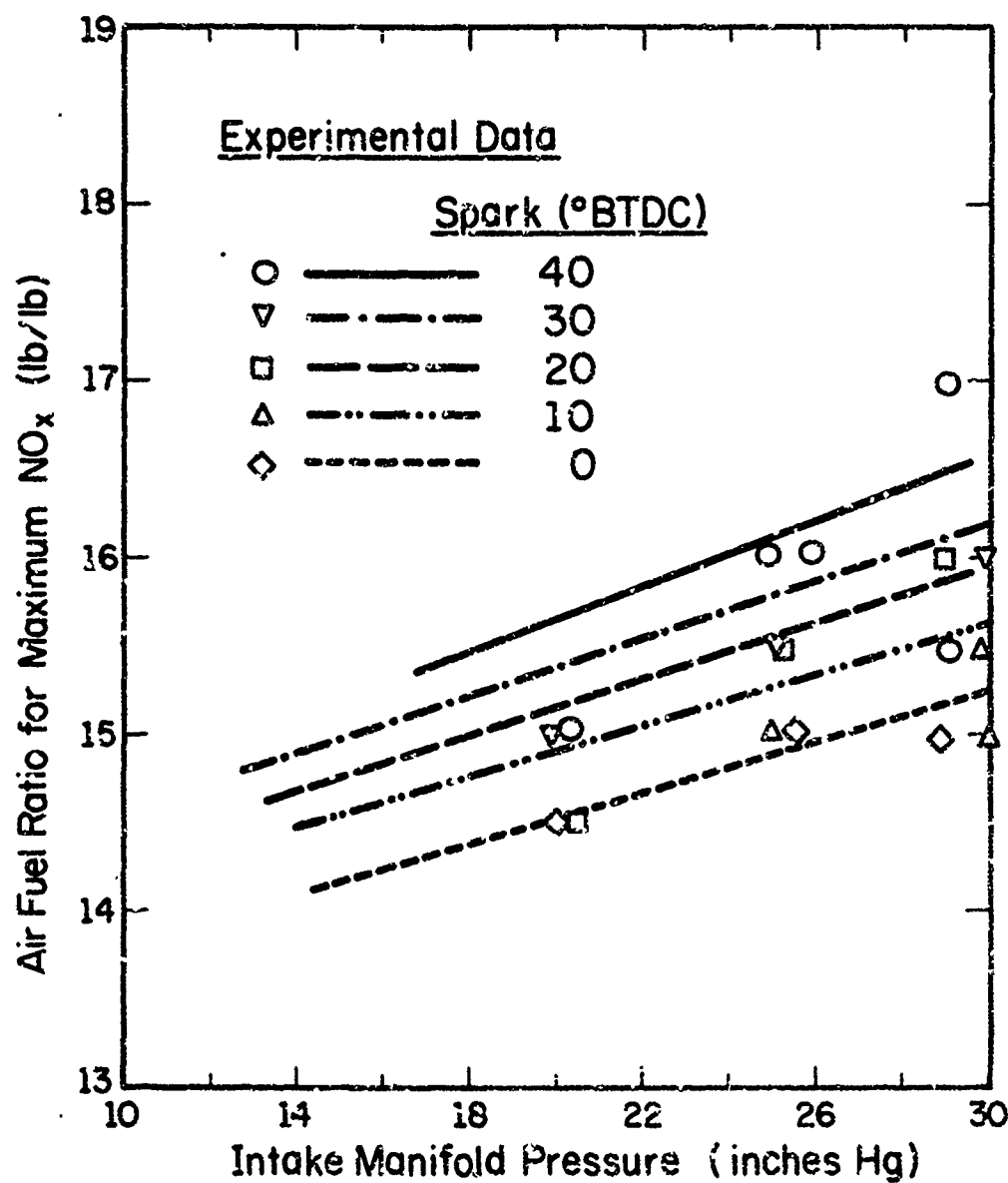


Figure 4 Maximum Oxides of Nitrogen Concentration vs. Intake Pressure for Spark Ignition Engines

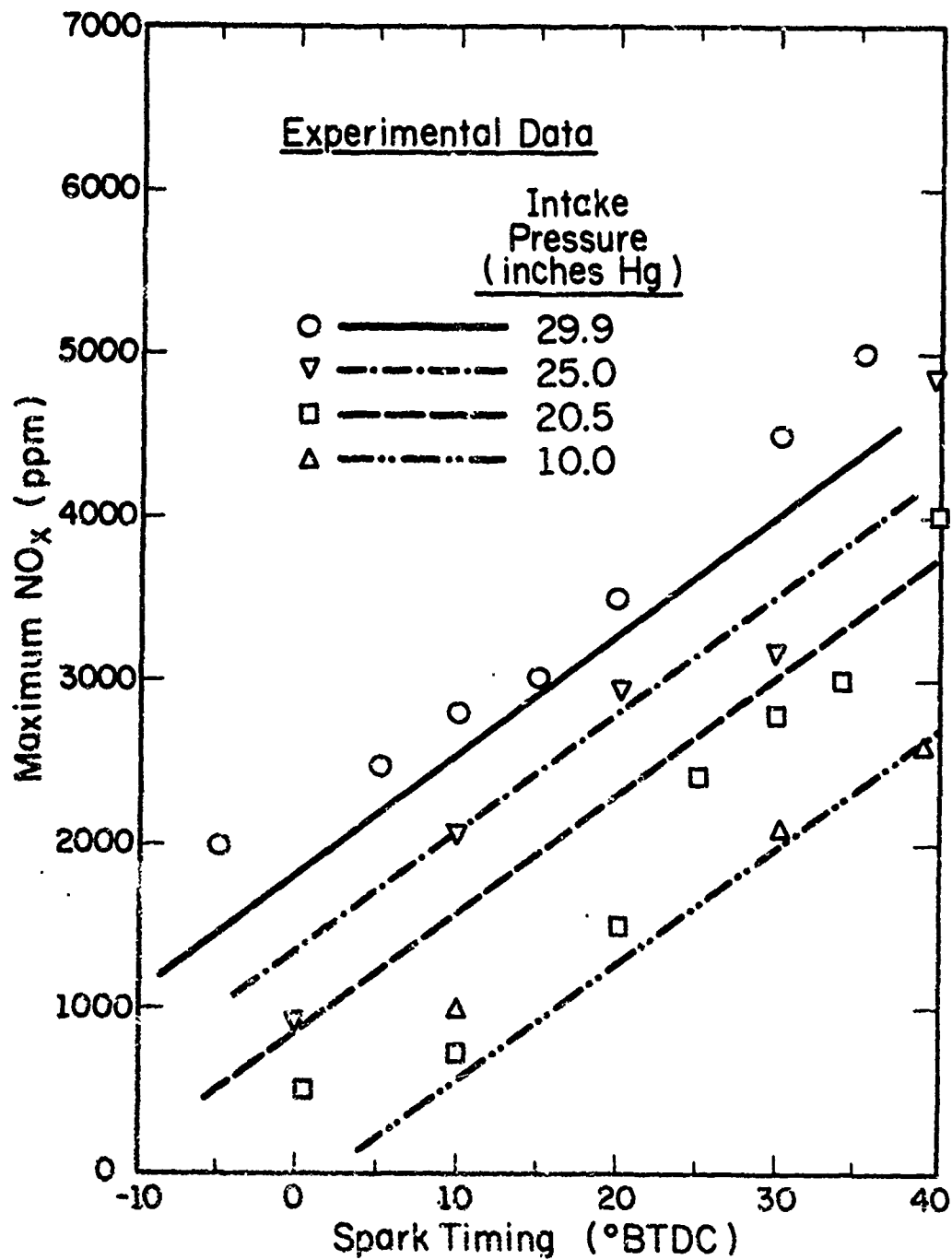


Figure 5 Maximum Oxides of Nitrogen Concentration vs. Spark Timing for Spark Ignition Engines

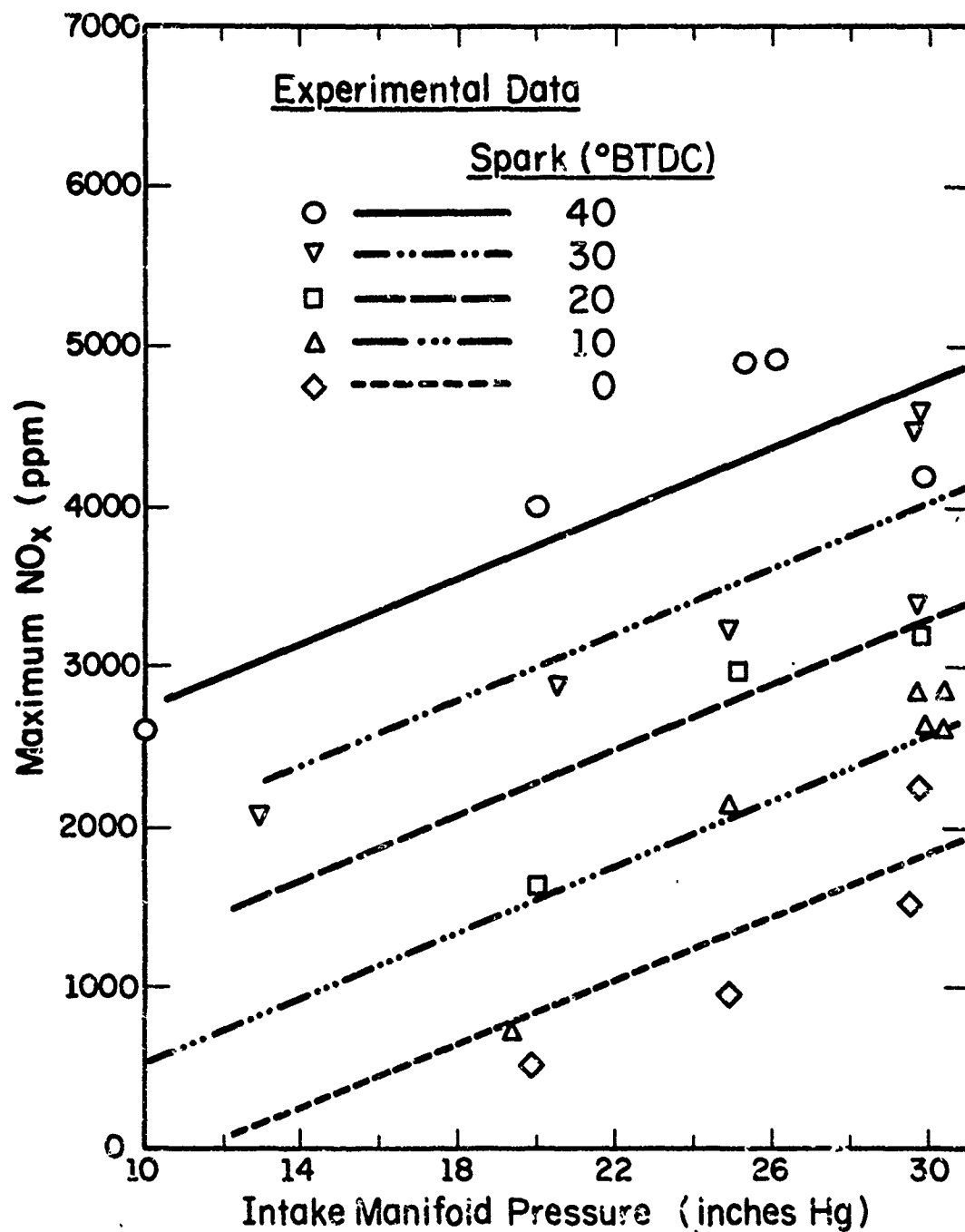


Figure 6 Air Fuel Ratio of Maximum Oxides of Nitrogen Concentration vs. Intake Pressure for Spark Ignition Engines

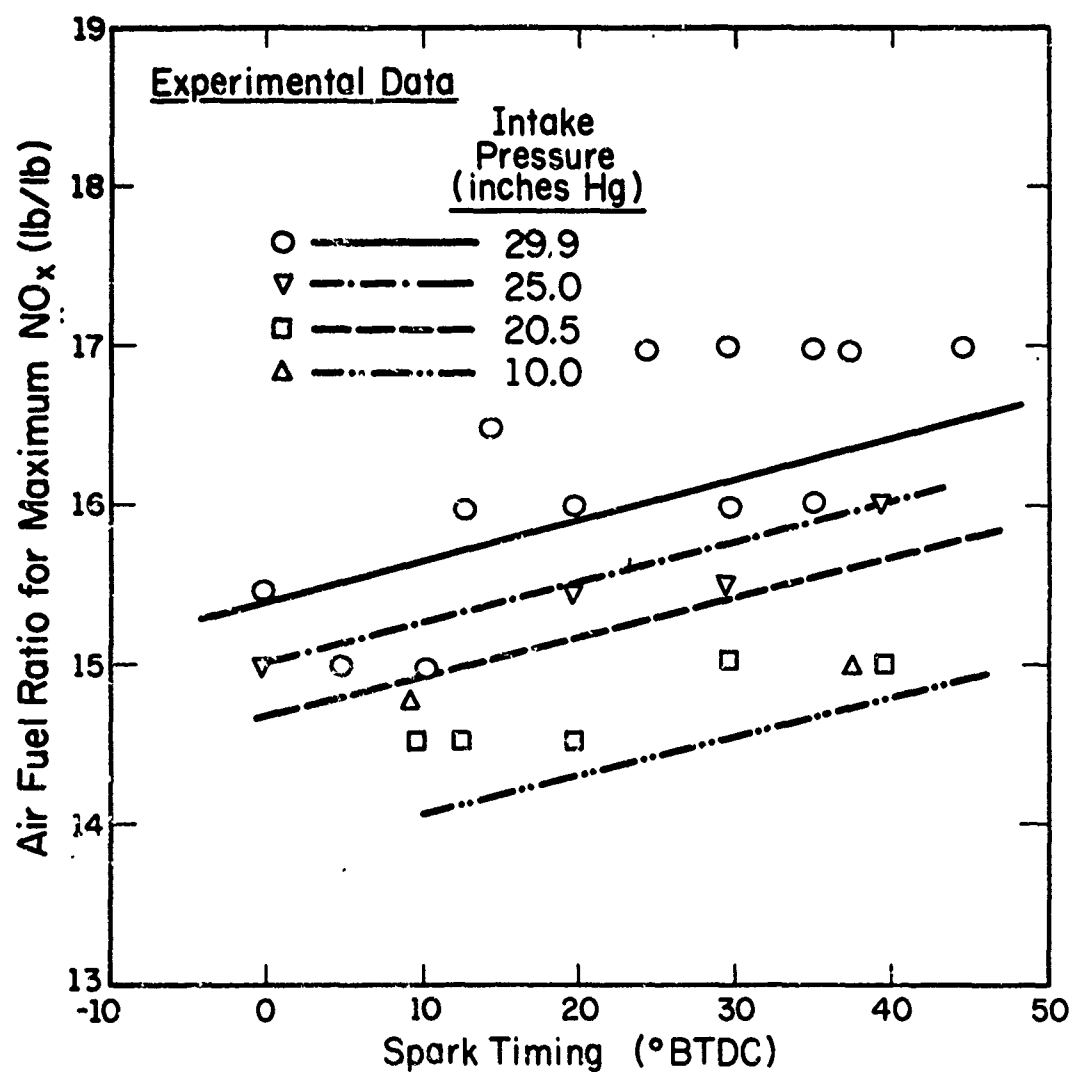


Figure 7 Air Fuel Ratio of Maximum Oxides of Nitrogen Concentration vs. Spark Timing for Spark Ignition Engines

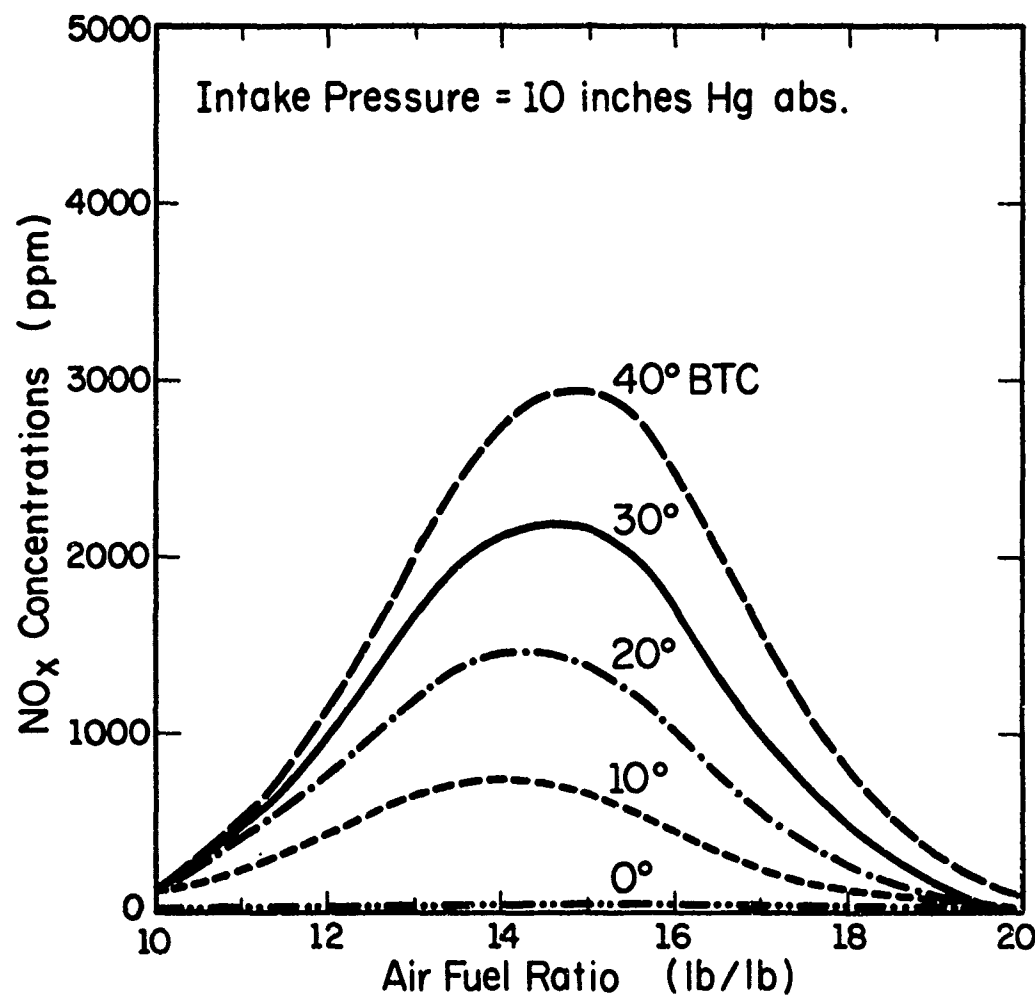


Figure 8 Predicted Spark Ignition Engine Oxides of Nitrogen Concentration vs. Air Fuel Ratio and Spark Timing

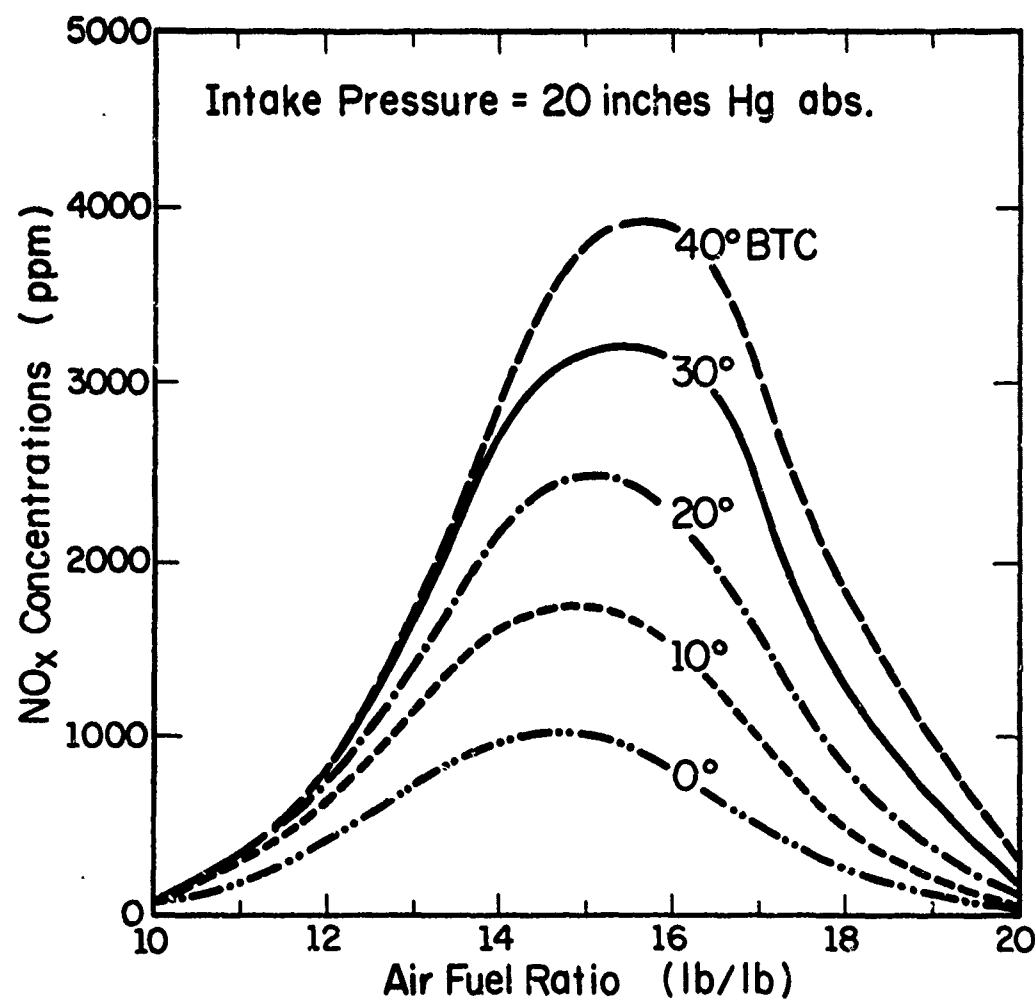


Figure 9 Predicted Spark Ignition Engine Oxides of Nitrogen Concentration vs. Air Fuel Ratio and Spark Timing

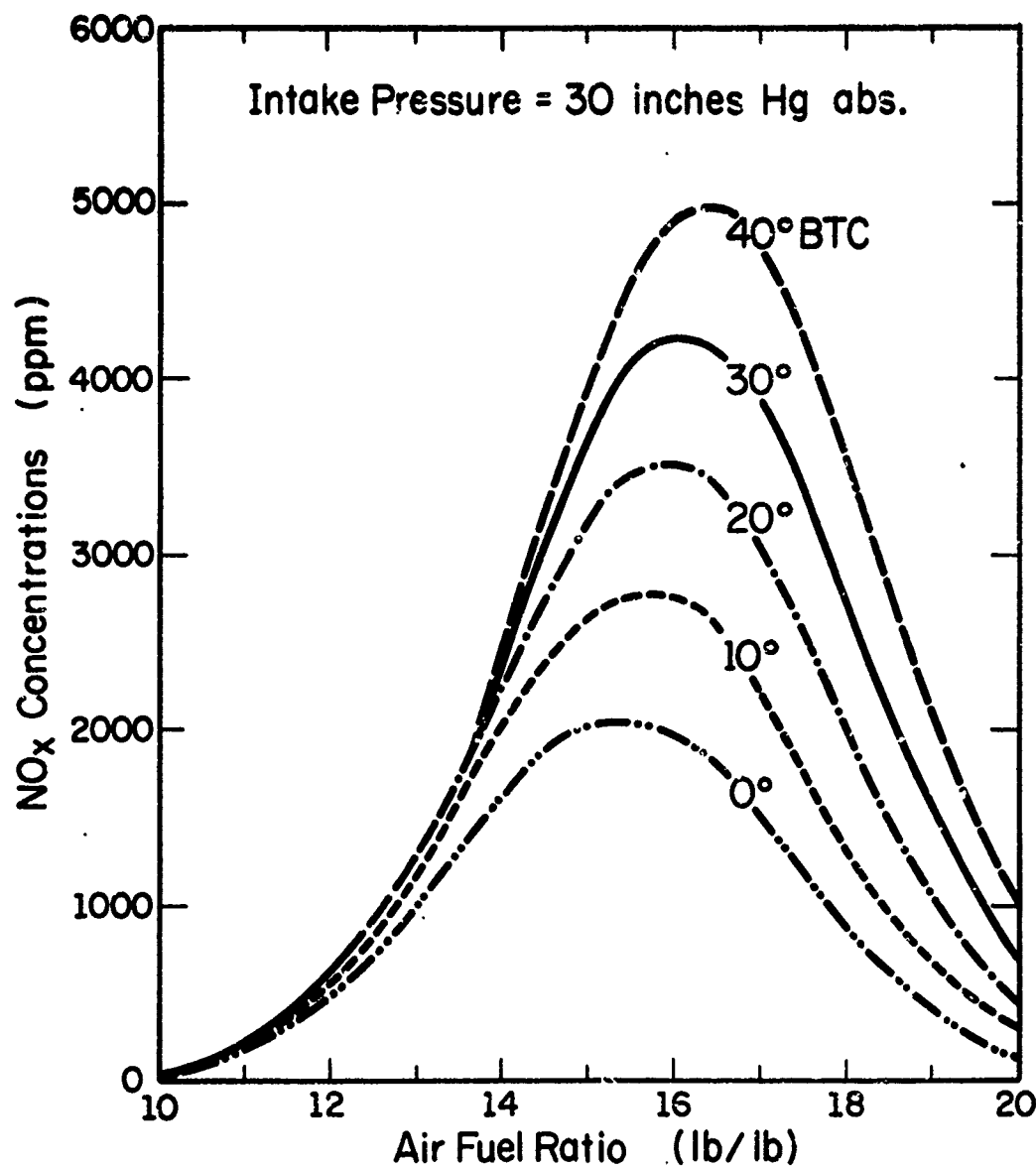


Figure 10 Predicted Spark Ignition Engine Oxides of Nitrogen Concentration vs. Air Fuel Ratio and Spark Timing

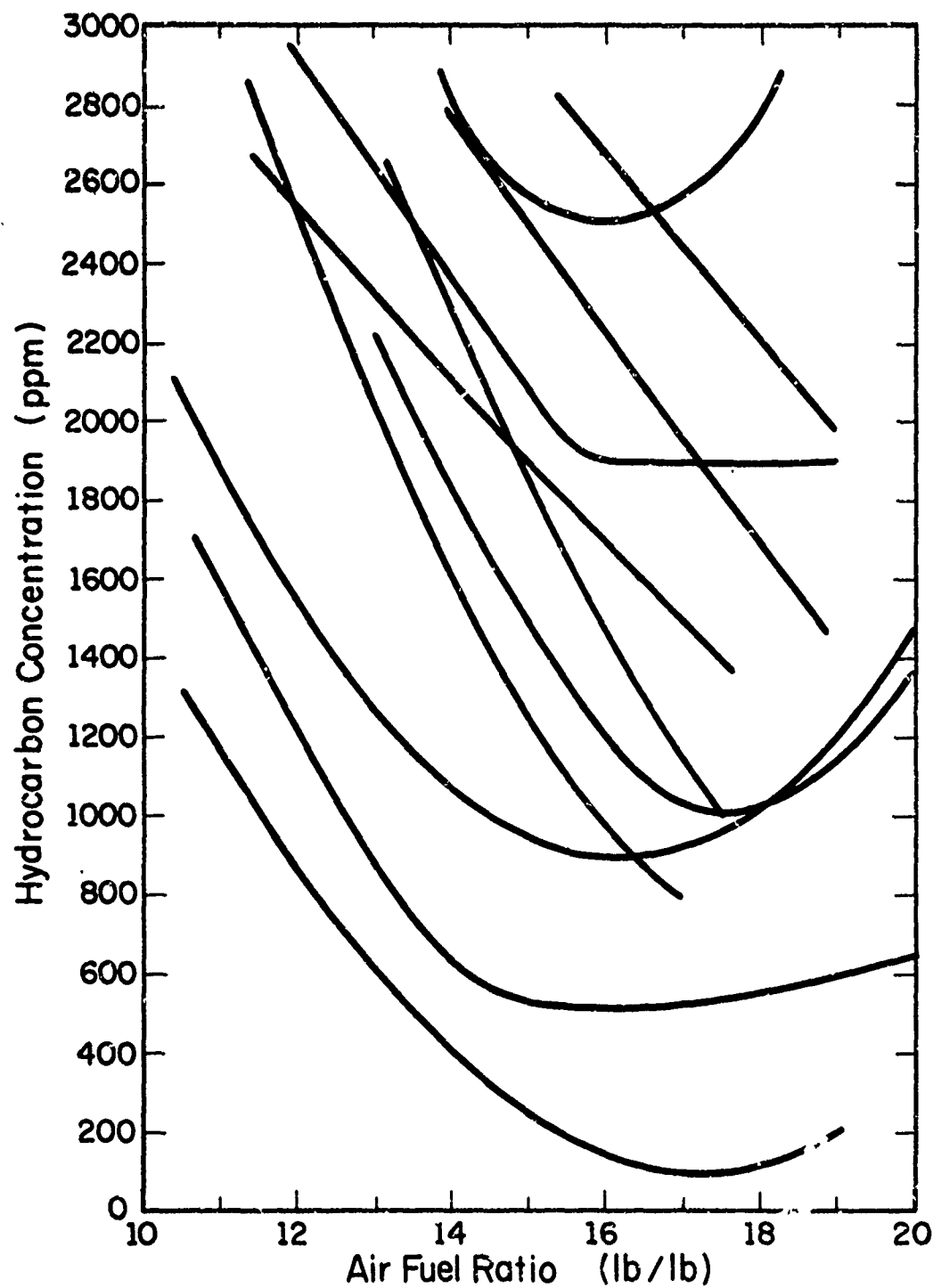


Figure 11 Typical Experimental Hydrocarbon Concentration vs. Air Fuel Ratio for Spark Ignition Engines

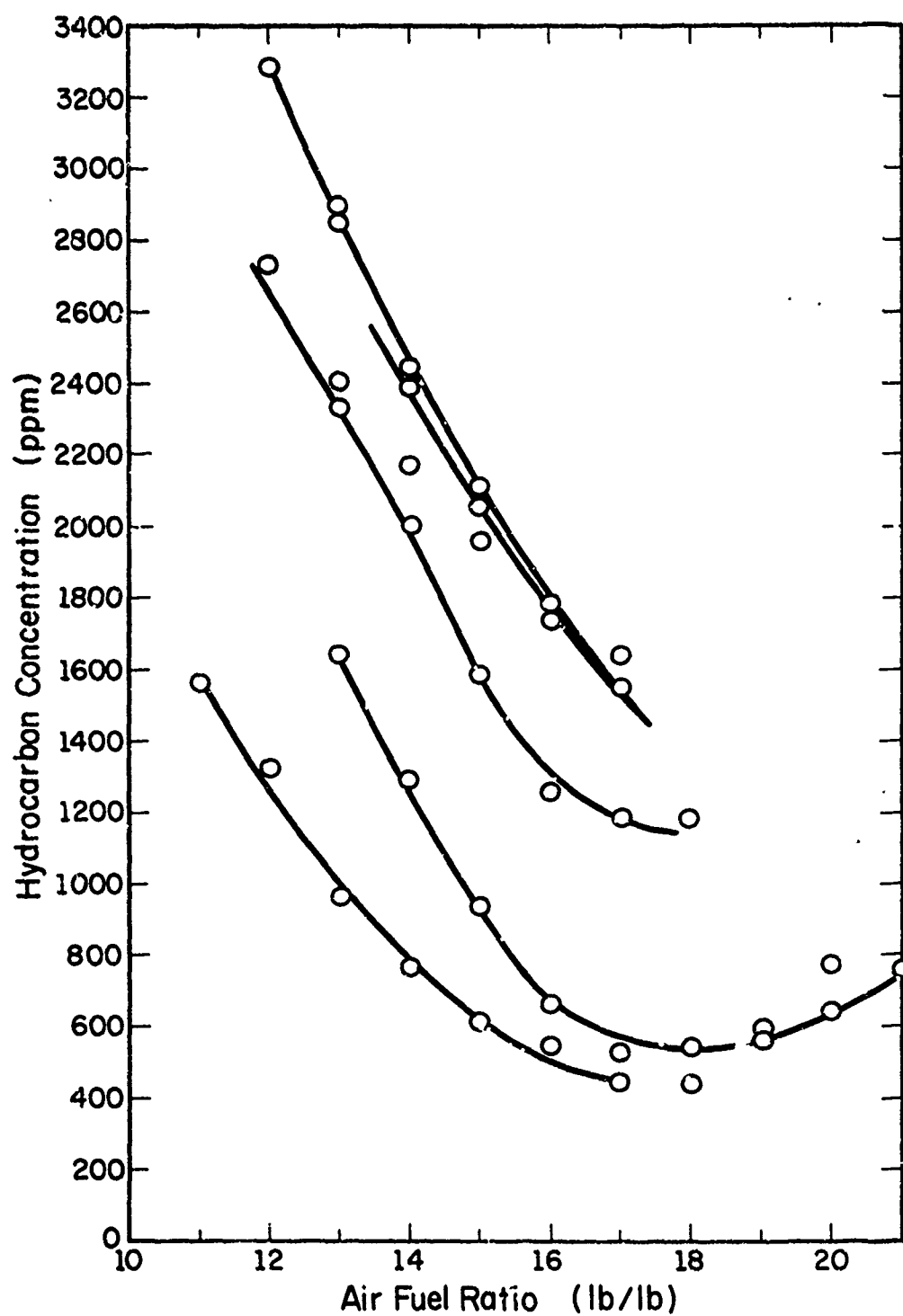


Figure 12 Corrected Hydrocarbon Concentrations *vs.* Air Fuel Ratio for Spark Ignition Engines

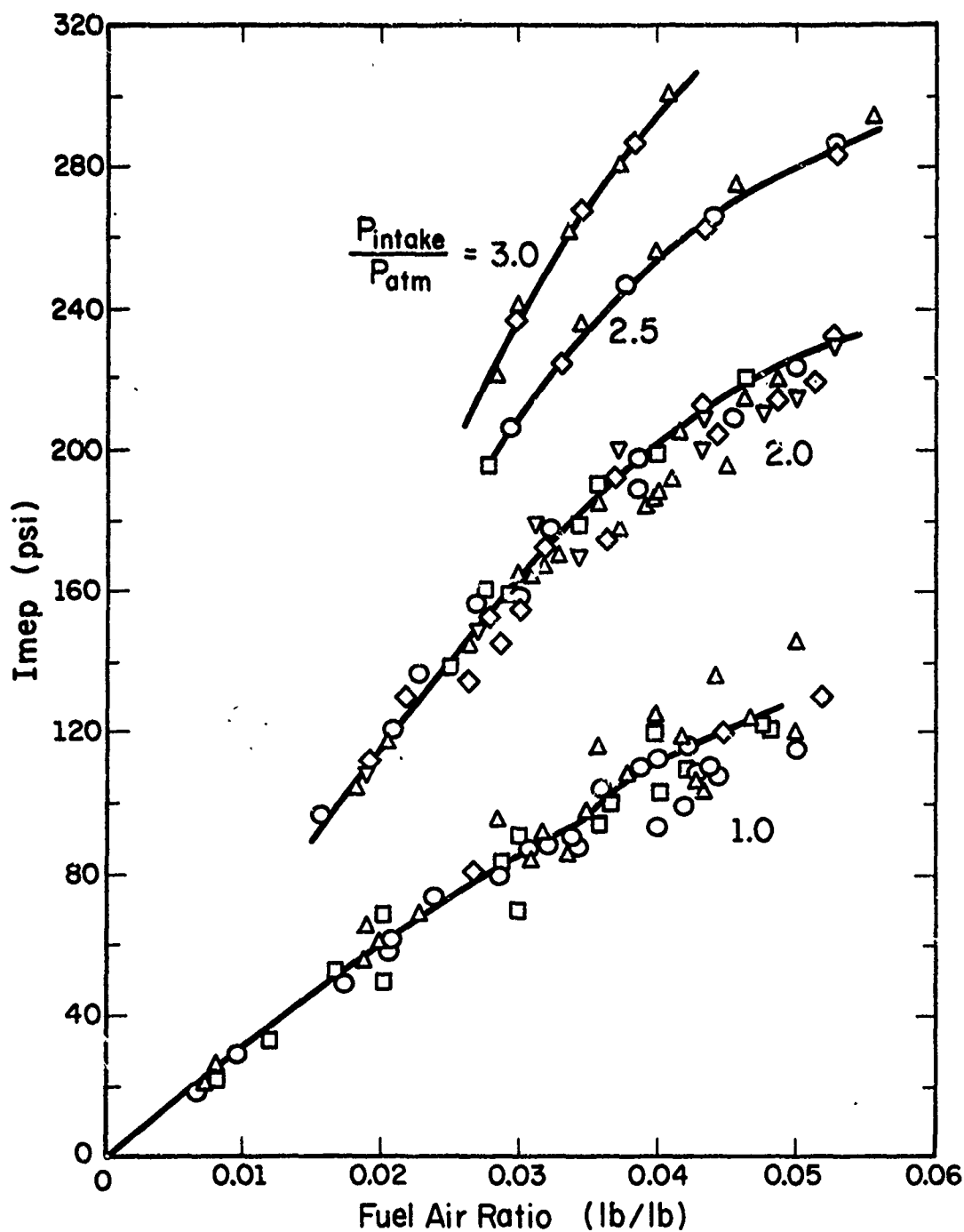


Figure 13 Indicated Mean Effective Pressure vs. Fuel Air Ratio for Compression Ignition Engines

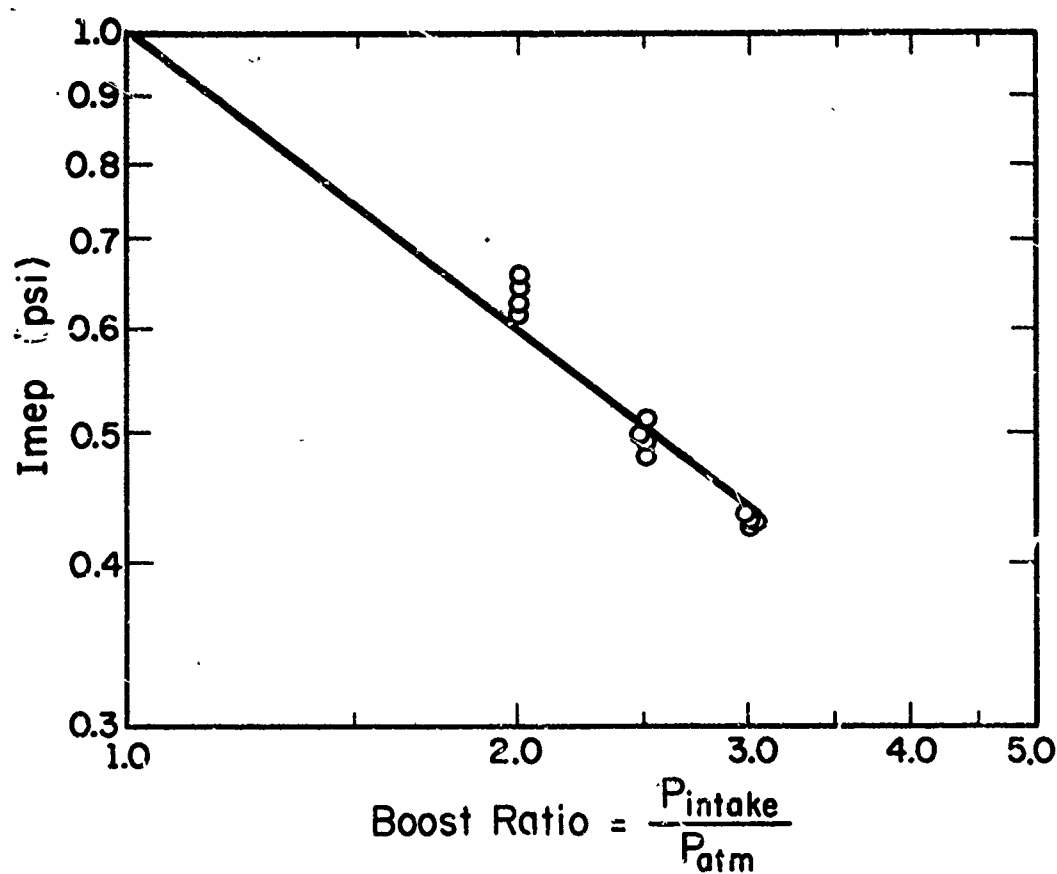


Figure 14 Correlation of Indicated Mean Effective Pressure with Boost for Turbocharged Compression Ignition Engines

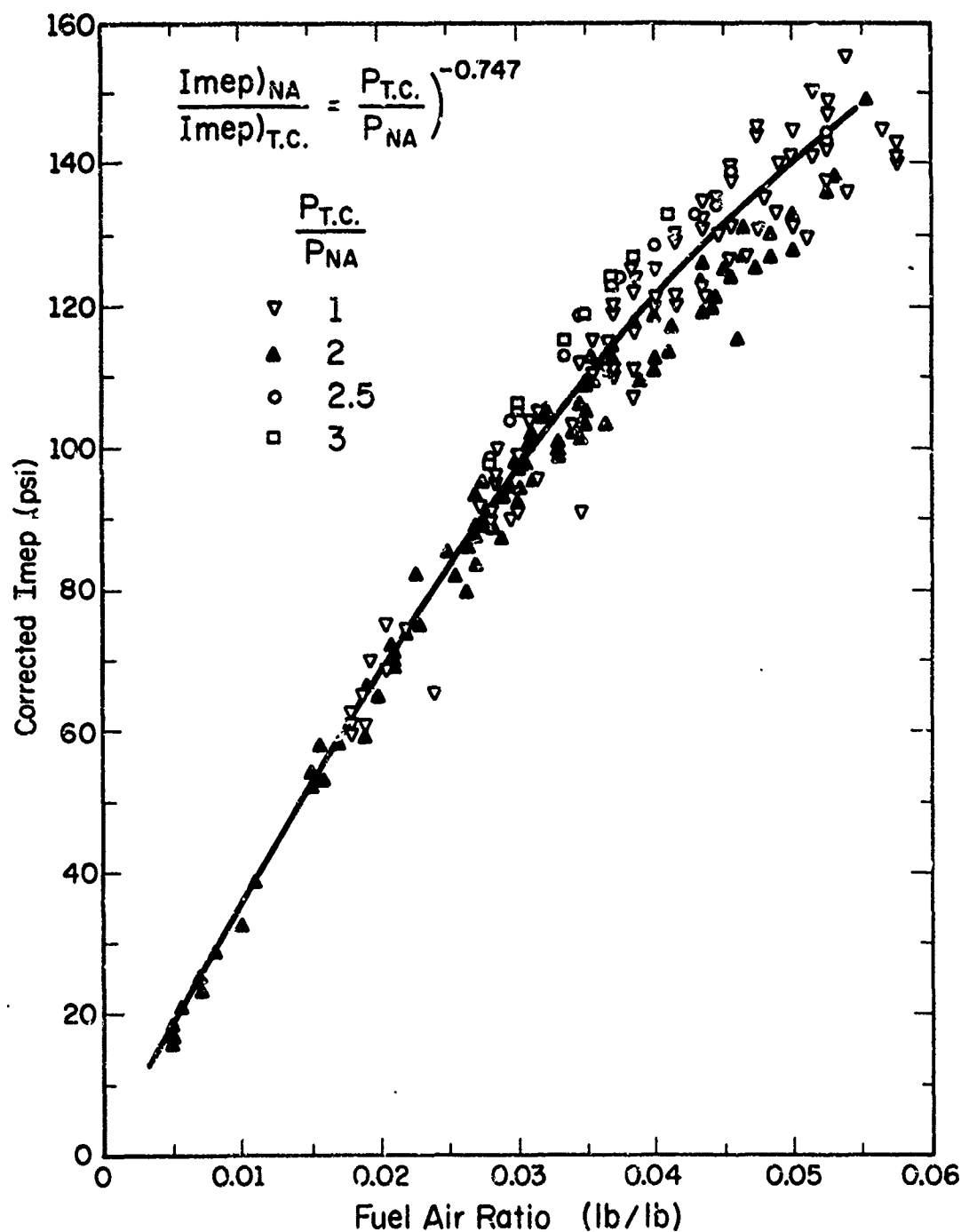


Figure 15 Corrected Indicated Mean Effective Pressure vs. Fuel Air Ratio for Compression Ignition Engines

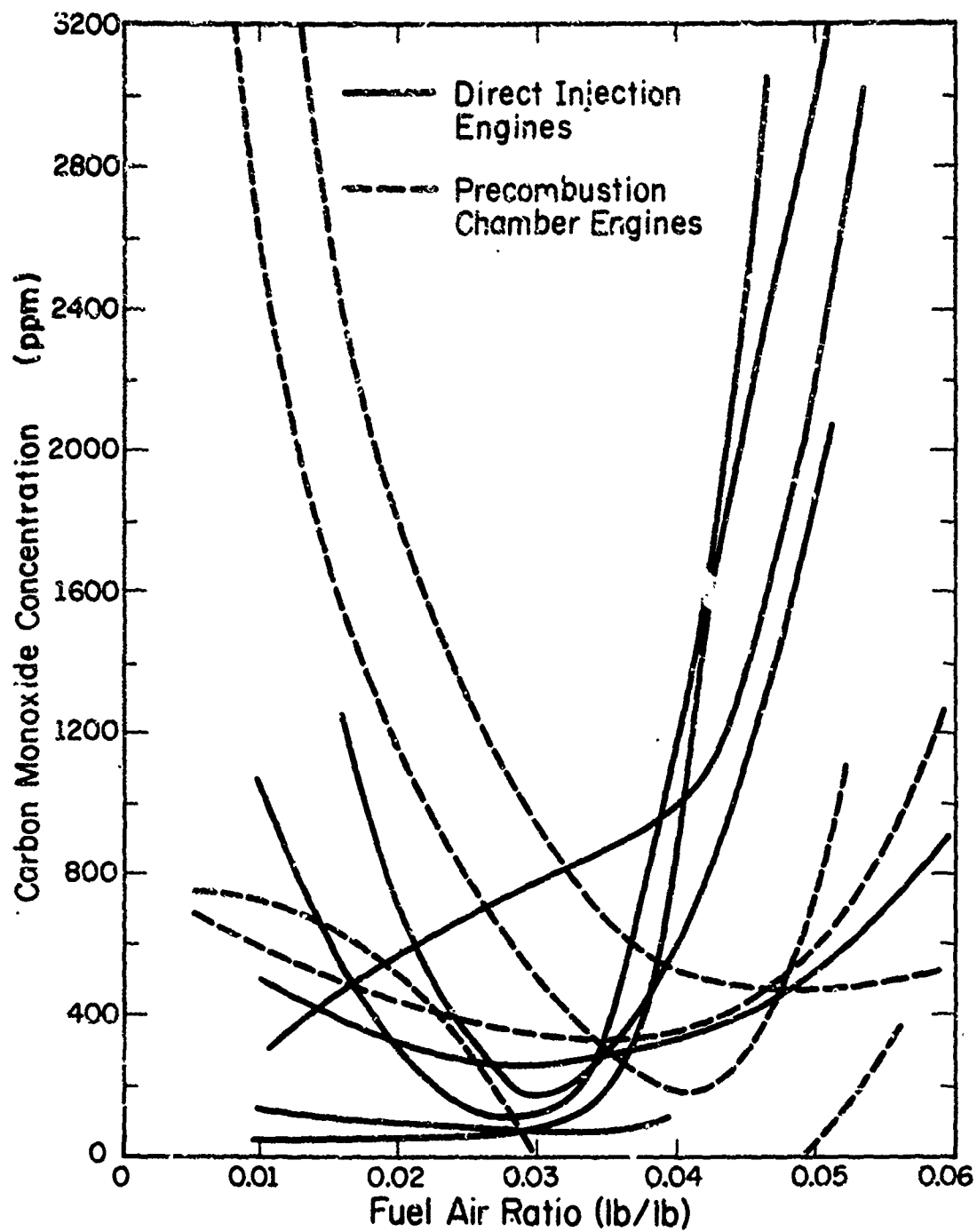


Figure 16 Typical Carbon Monoxide Concentrations vs. Fuel Air Ratio for Compression Ignition Engines

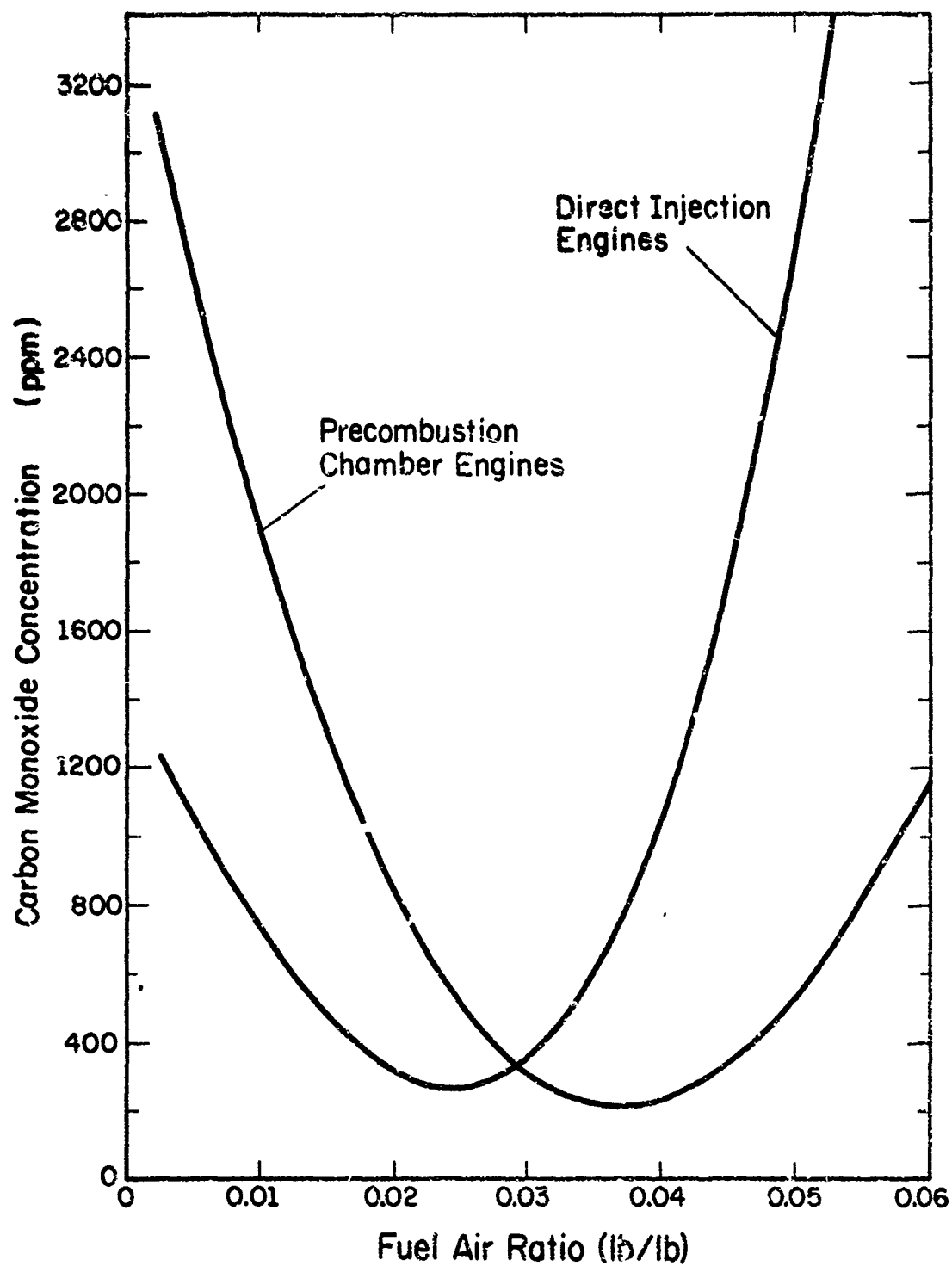


Figure 17 Predicted Carbon Monoxide Concentration vs. Fuel Air Ratio for Compression Ignition Engines

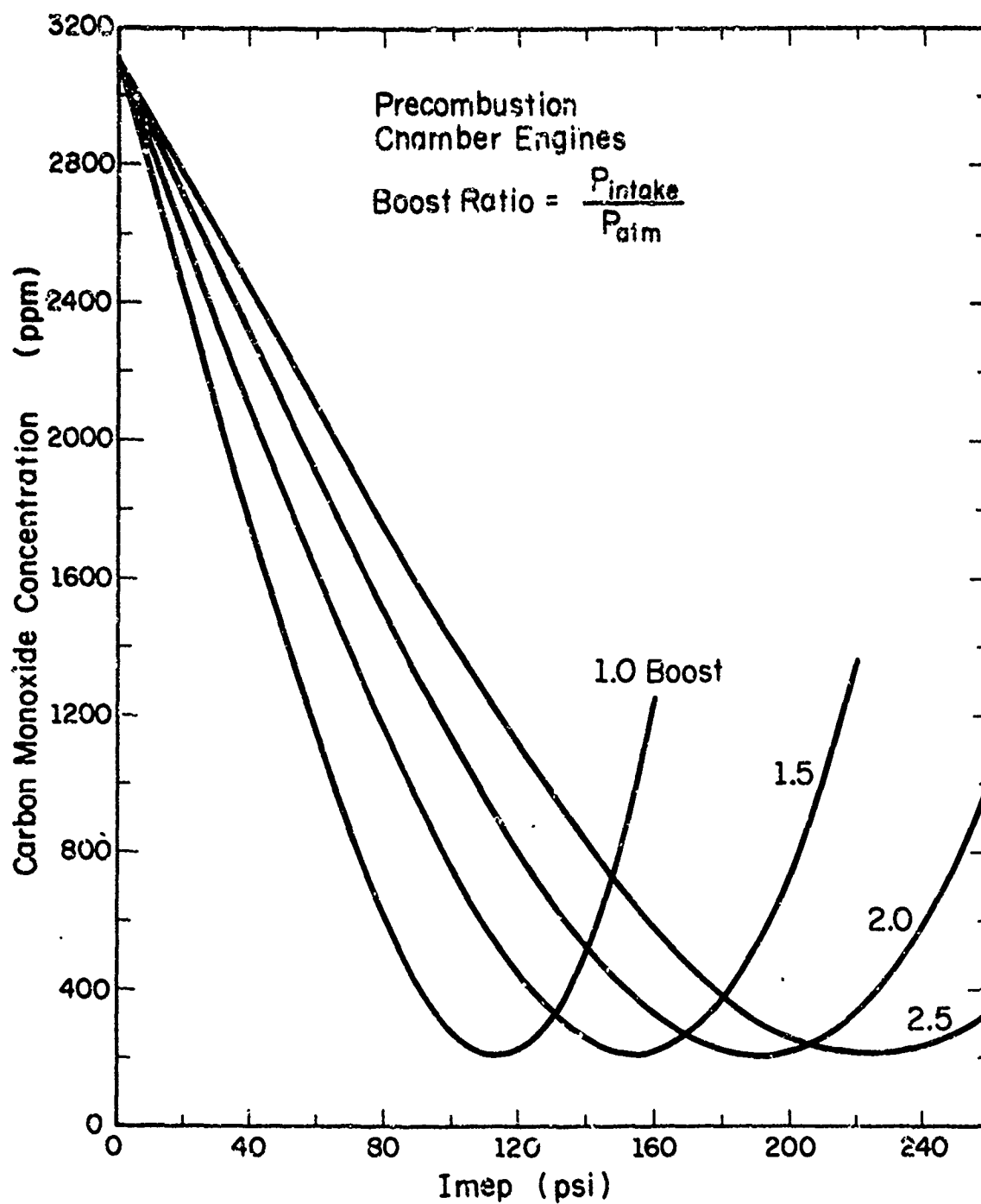


Figure 18 Predicted Carbon Monoxide Concentration vs. Indicated Mean Effective Pressure for Precombustion Chamber Engines

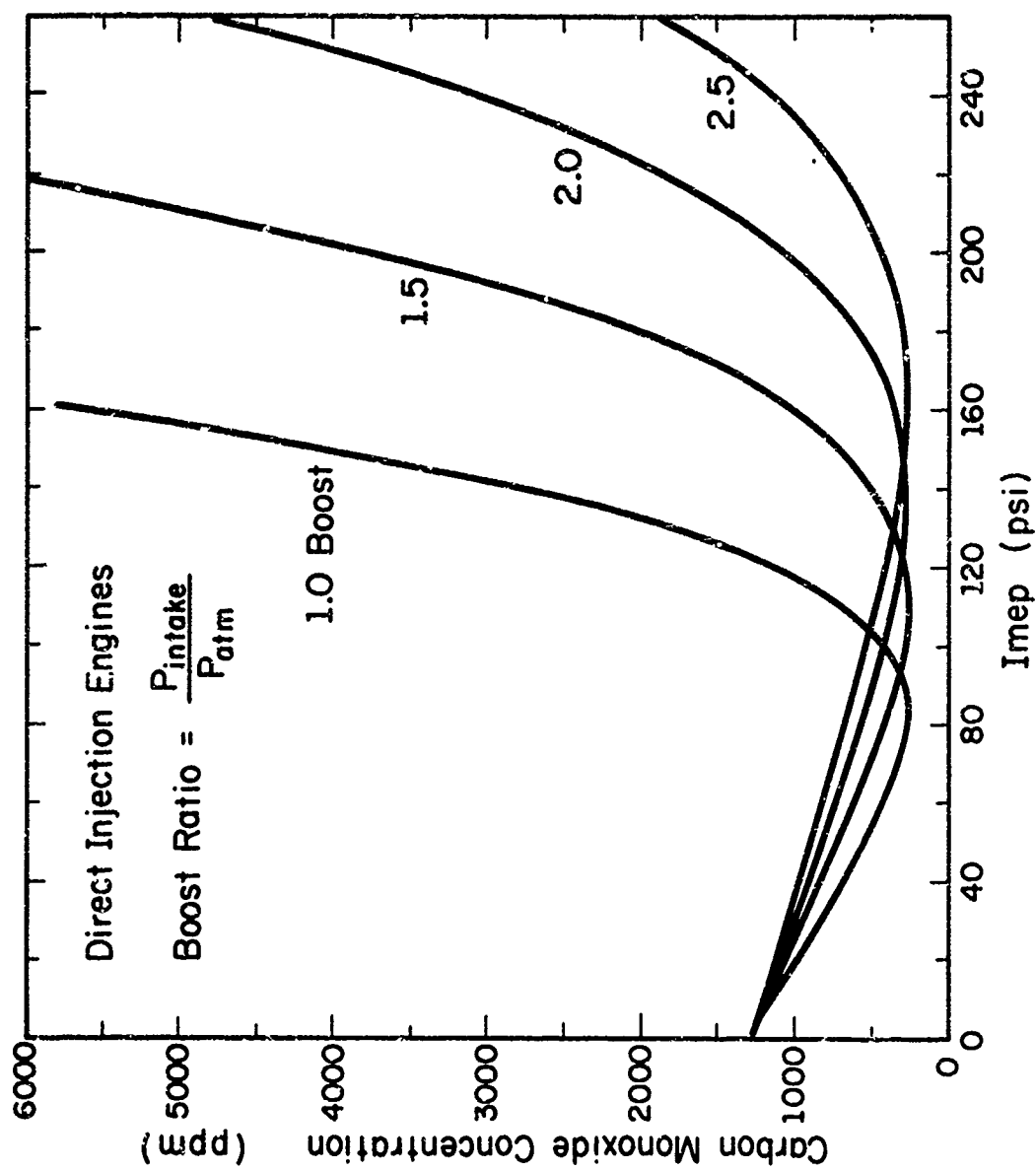


Figure 19 Predicted Carbon Monoxide Concentration vs. Indicated Mean Effective Pressure for Direct Injection Engines

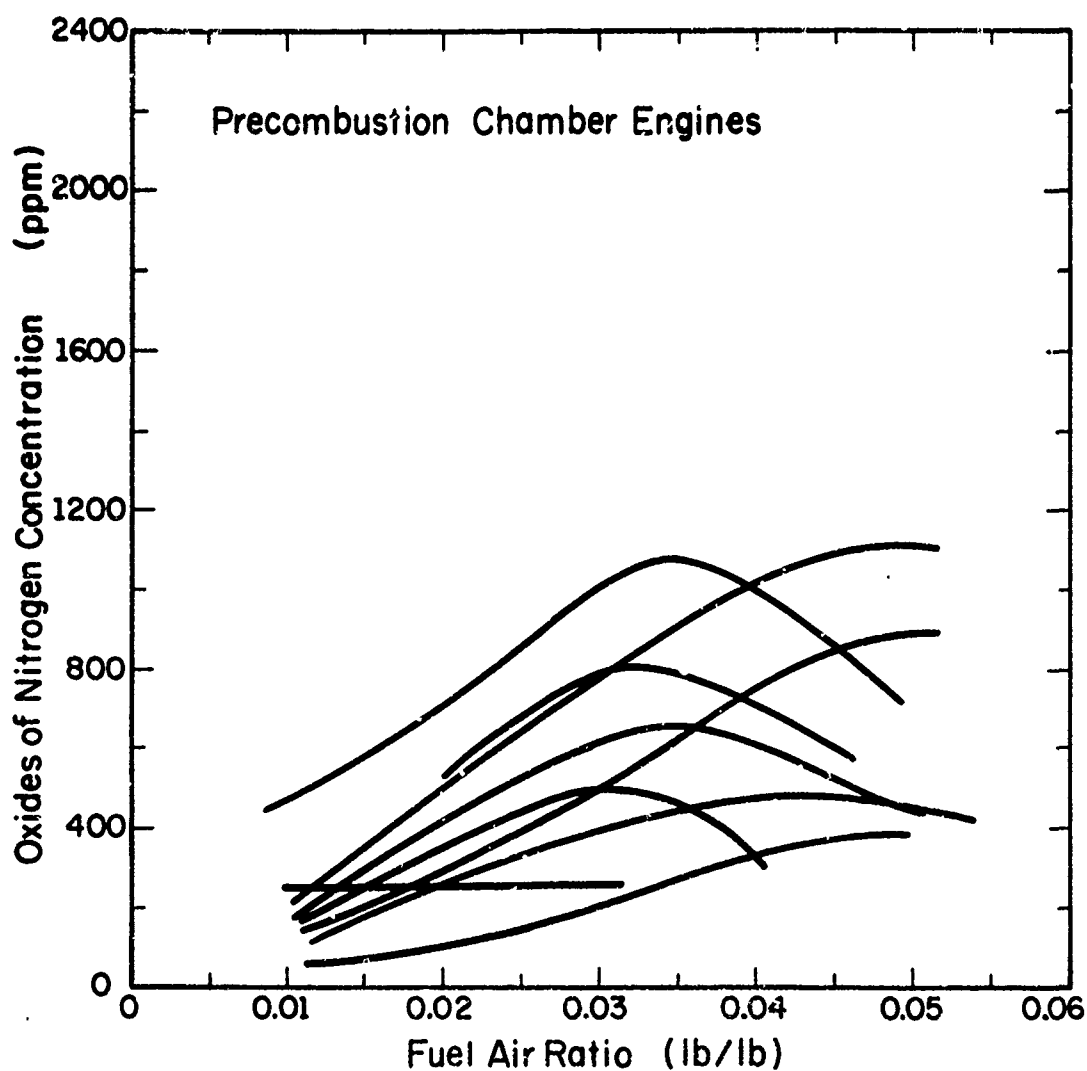


Figure 20 Experimental Oxides of Nitrogen Concentration vs. Fuel Air Ratio for Precombustion Chamber Engines

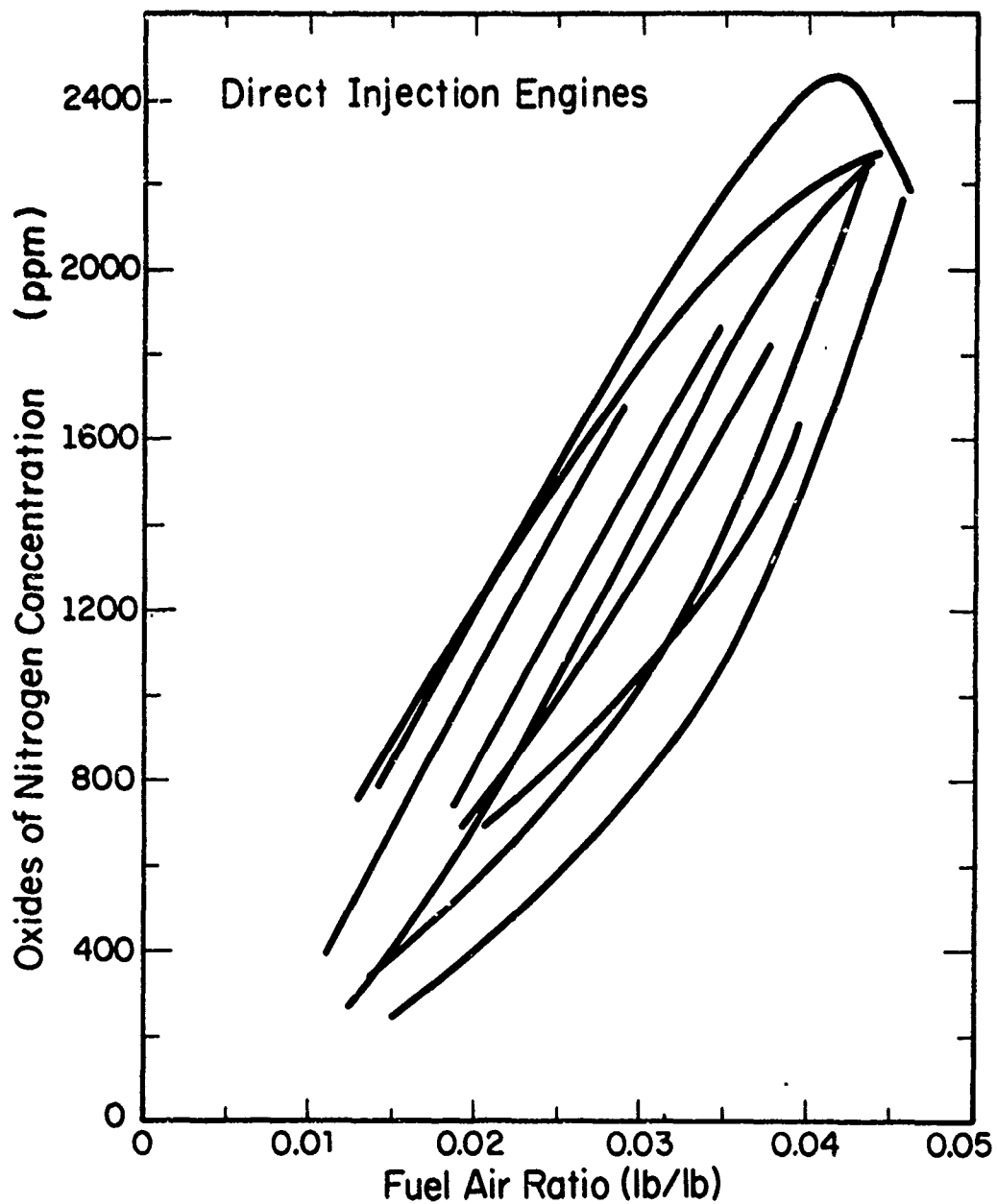


Figure 21 Experimental Oxides of Nitrogen Concentration *vs.* Fuel Air Ratio for Direct Injection Engines

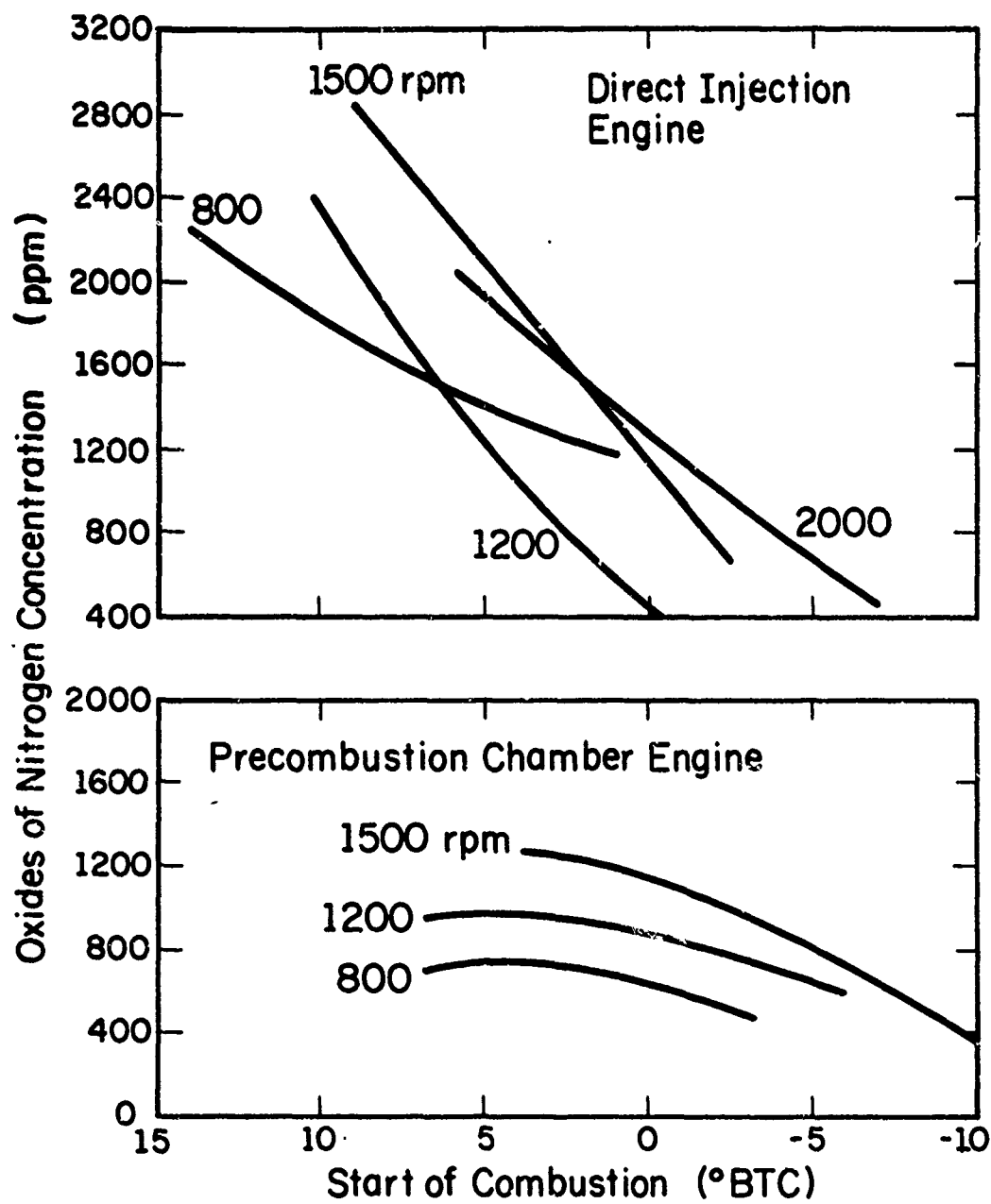


Figure 22 Effect of Injection Timing on Typical Compression Ignition Engine Oxides of Nitrogen Emissions

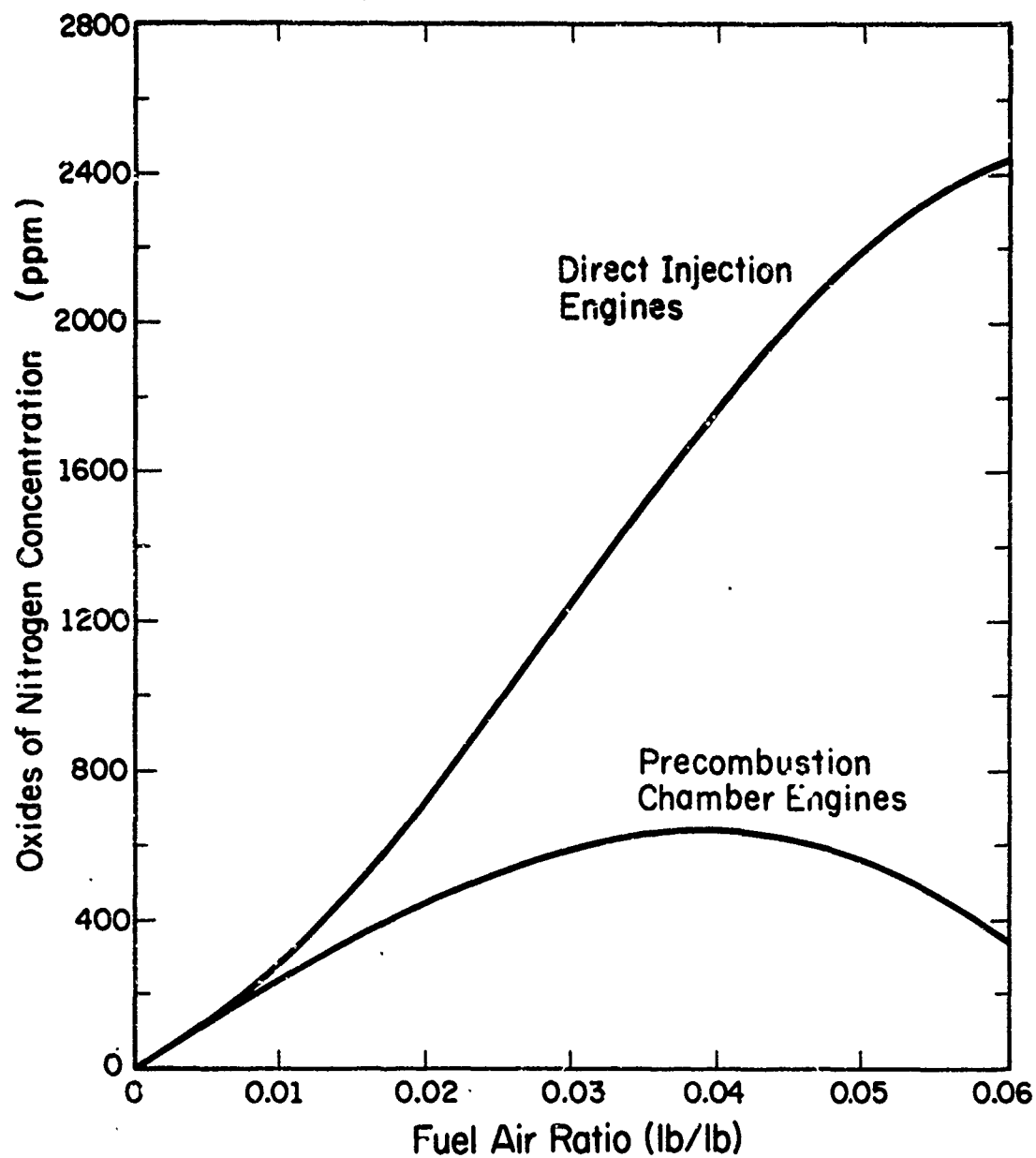


Figure 23 Predicted Oxides of Nitrogen Concentration *vs.* Fuel Air Ratio for Compression Ignition Engines

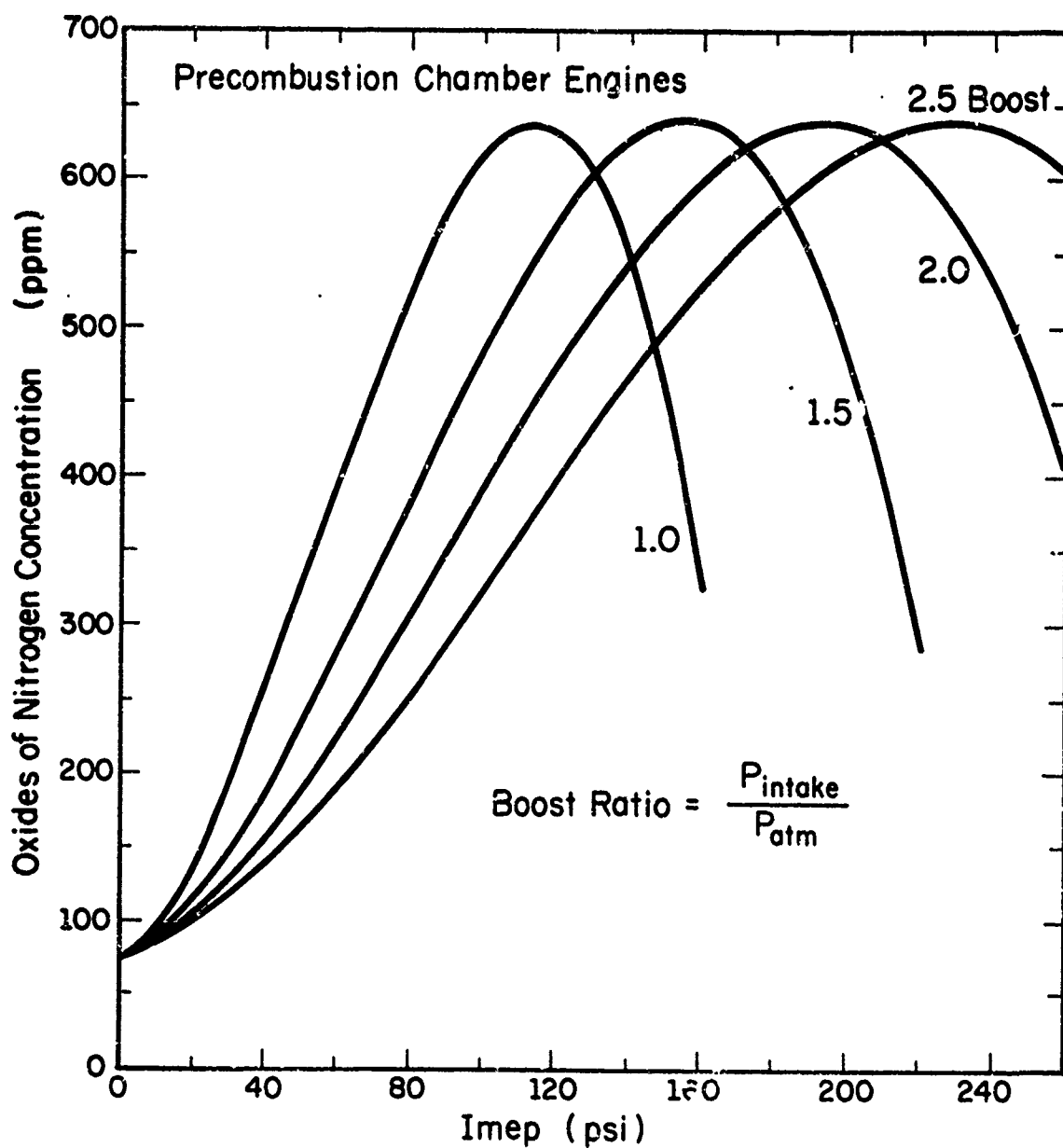


Figure 24 Predicted Oxides of Nitrogen Concentration *vs.* Indicated Mean Effective Pressure for Precombustion Chamber Engines

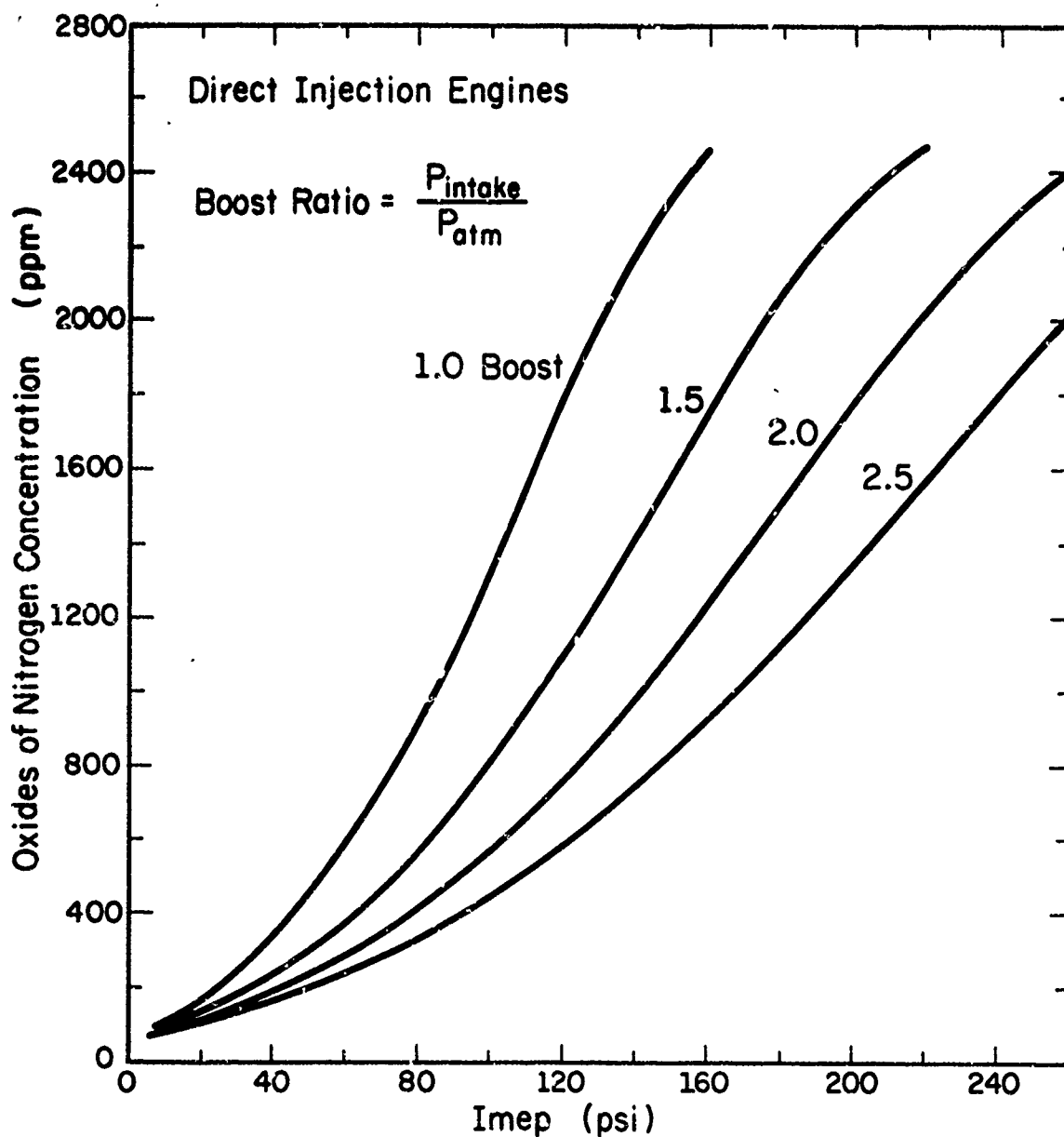


Figure 25 Predicted Oxides of Nitrogen Concentration *vs.* Indicated Mean Effective Pressure for Direct Injection Engines

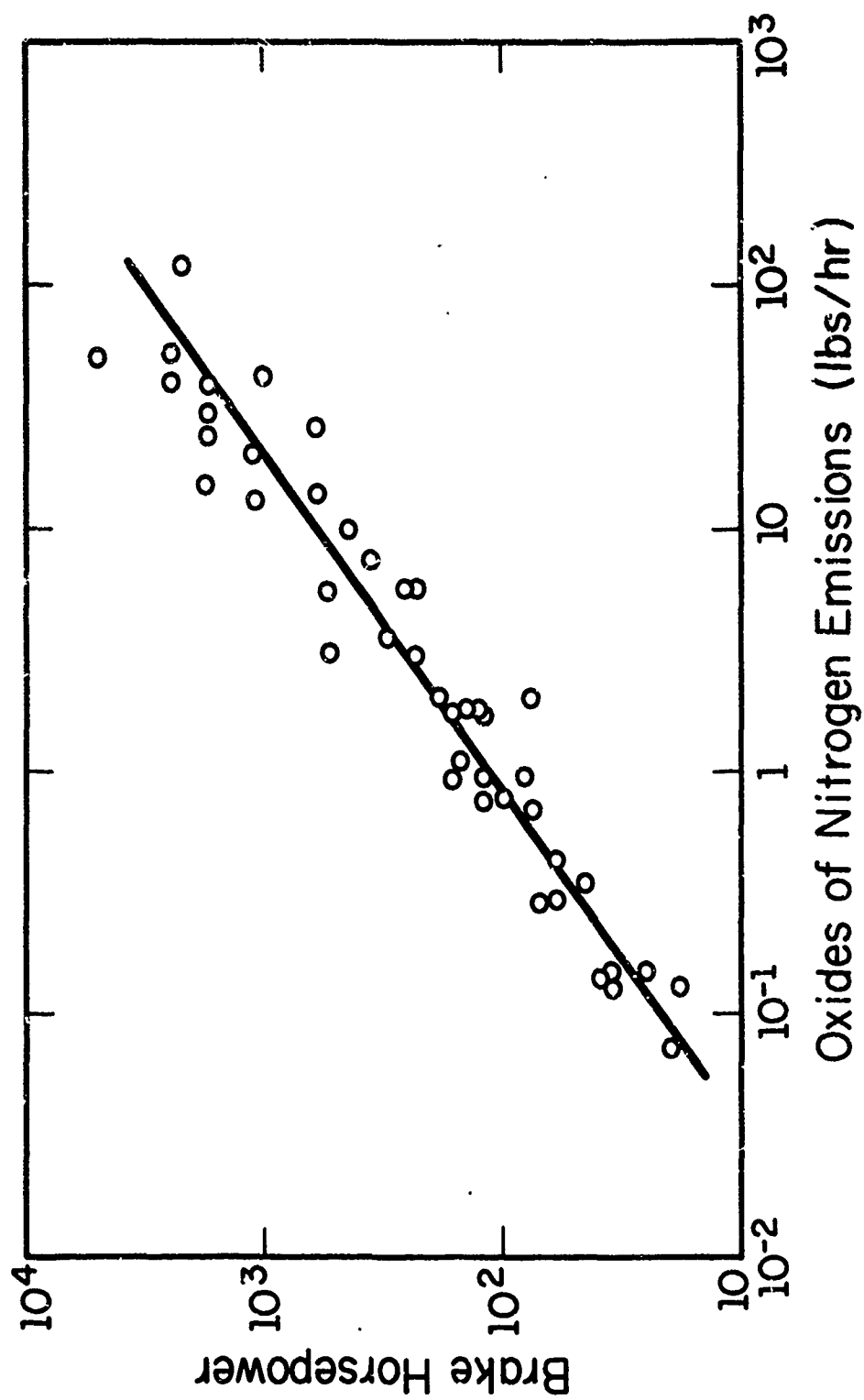


Figure 26 Mass Emission Rate of Oxides of Nitrogen vs. Compression Ignition Engine Brake Horsepower

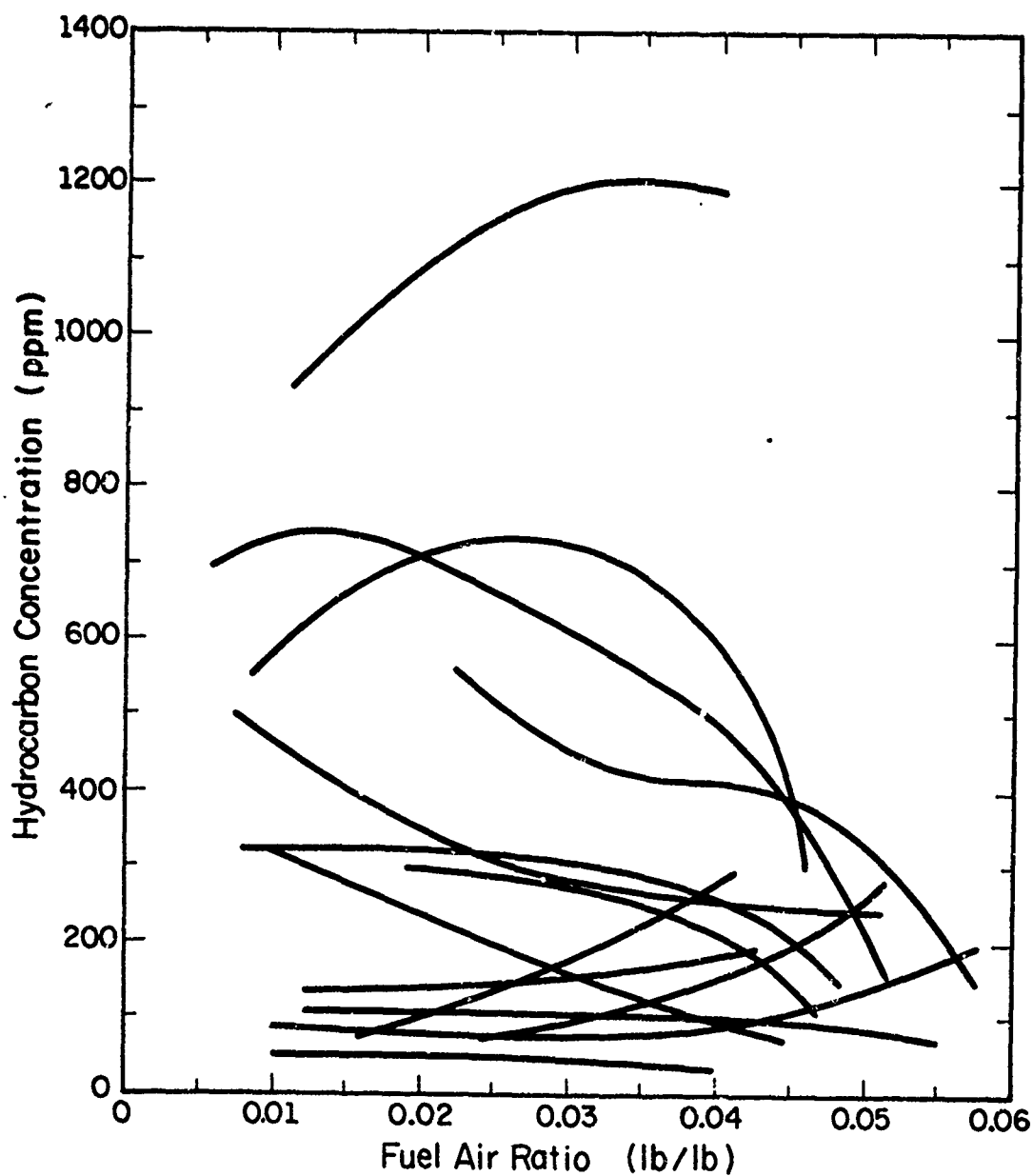


Figure 27 Experimental Hydrocarbon Concentration vs. Fuel Air Ratio for Compression Ignition Engines

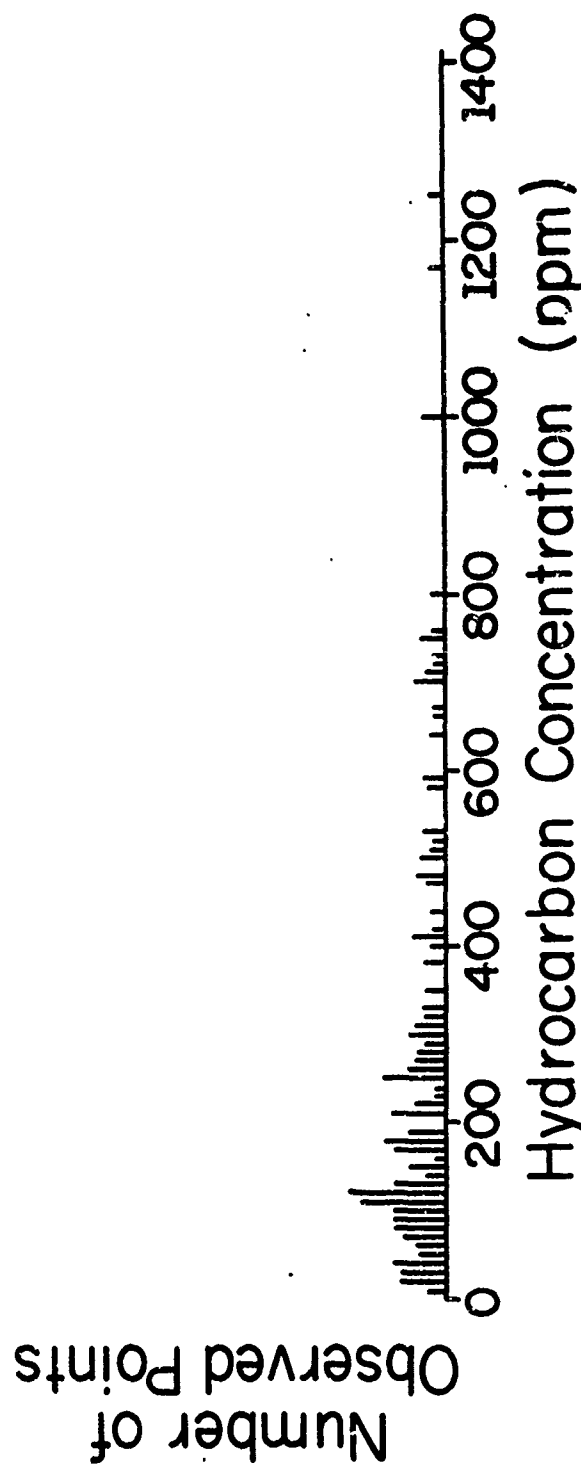


Figure 28 Frequency Distribution of Experimental Hydrocarbon Concentrations for Compression Ignition Engines

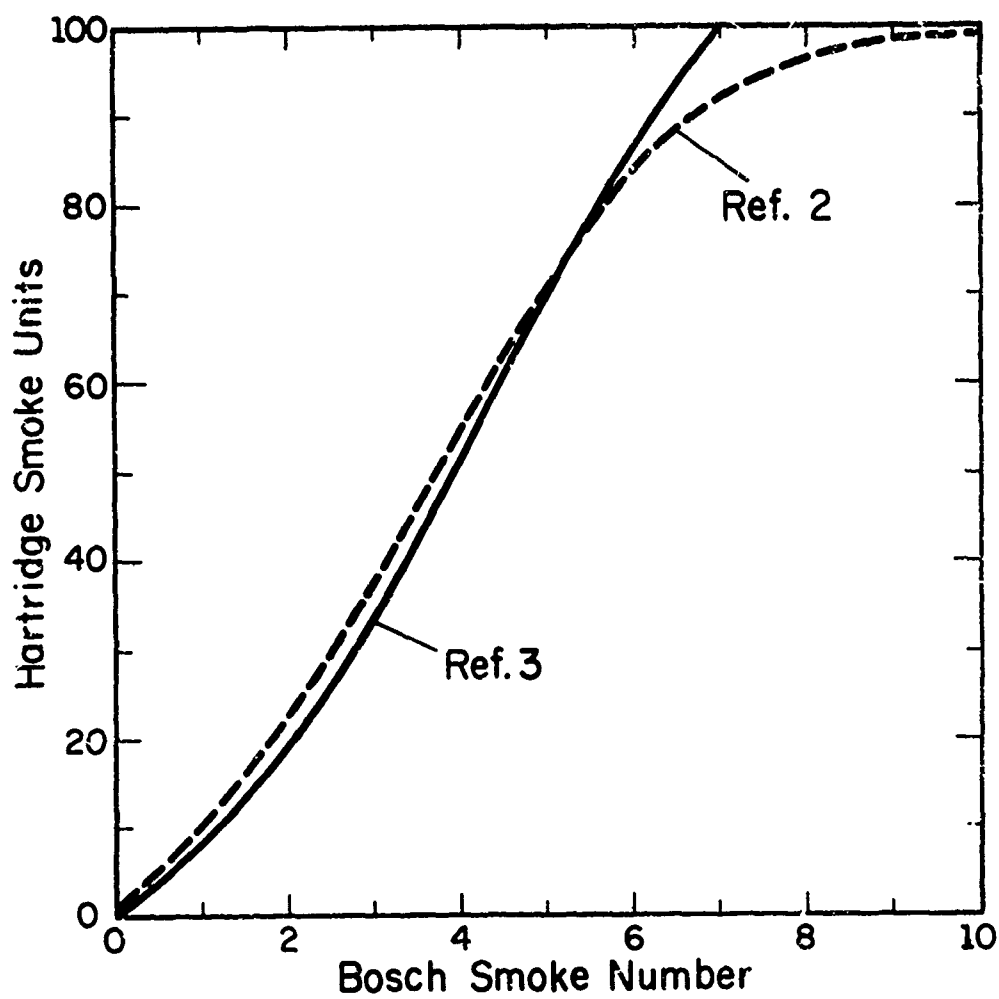


Figure 29 Correlation of Bosch Smokemeter with Hartridge Smokemeter

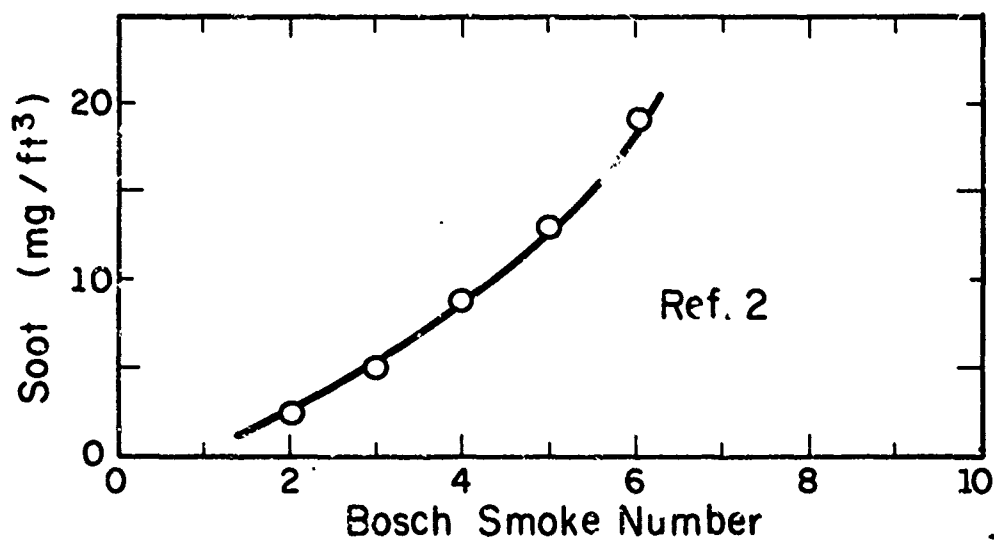
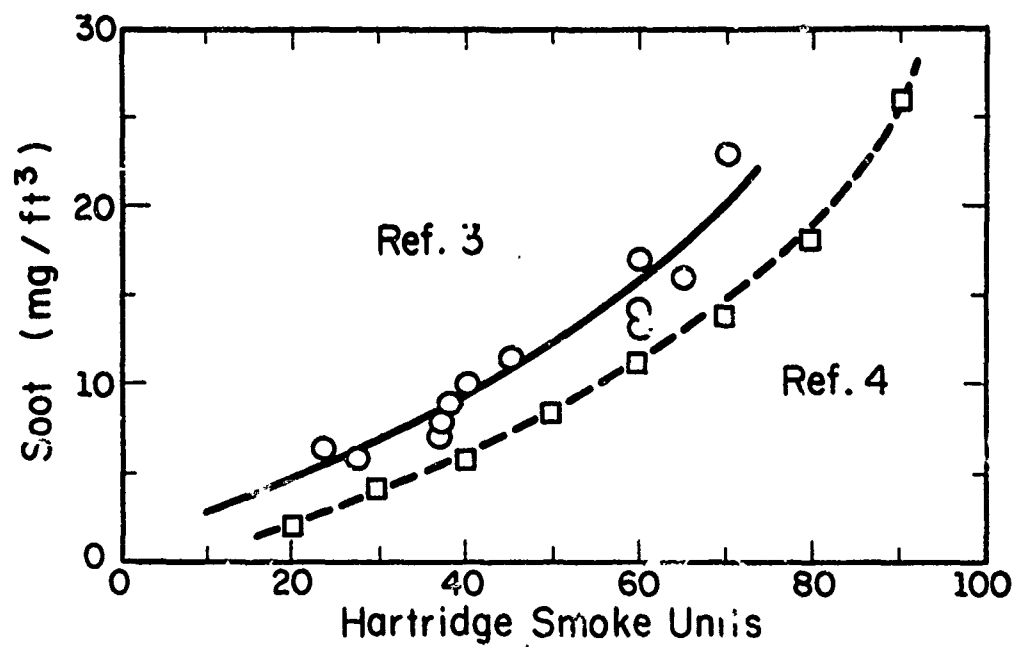


Figure 30 Correlation of Bosch and Hartridge Smokemeter Readings with Soot Concentration

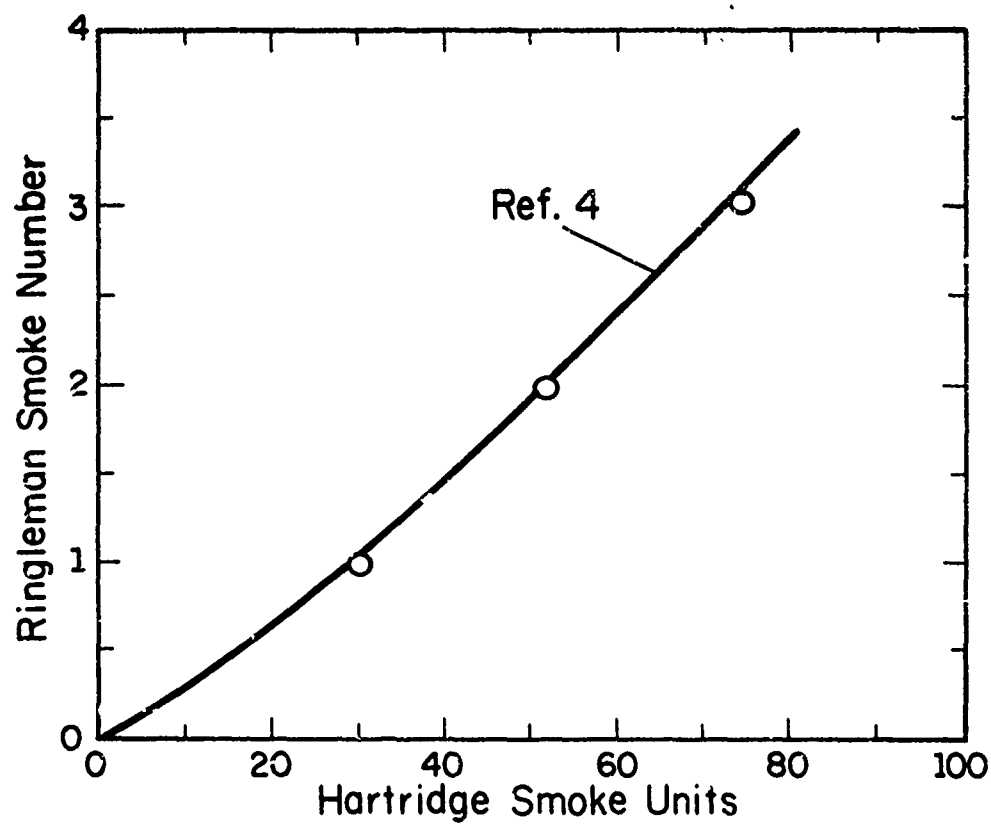


Figure 31 Correlation of Ringlemann Smoke Rating with Hartridge Smokemeter

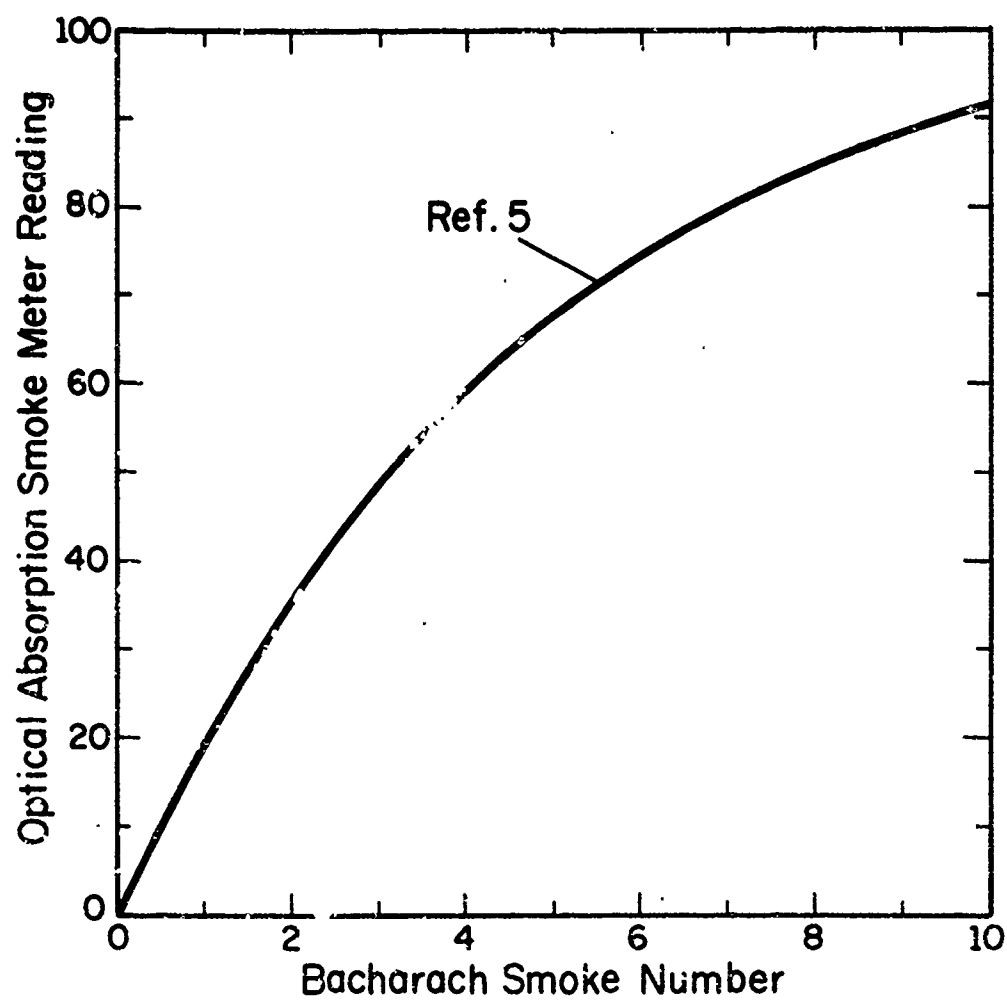


Figure 32 Correlation of Optical Absorption Smokemeter with Bacharach Smokemeter

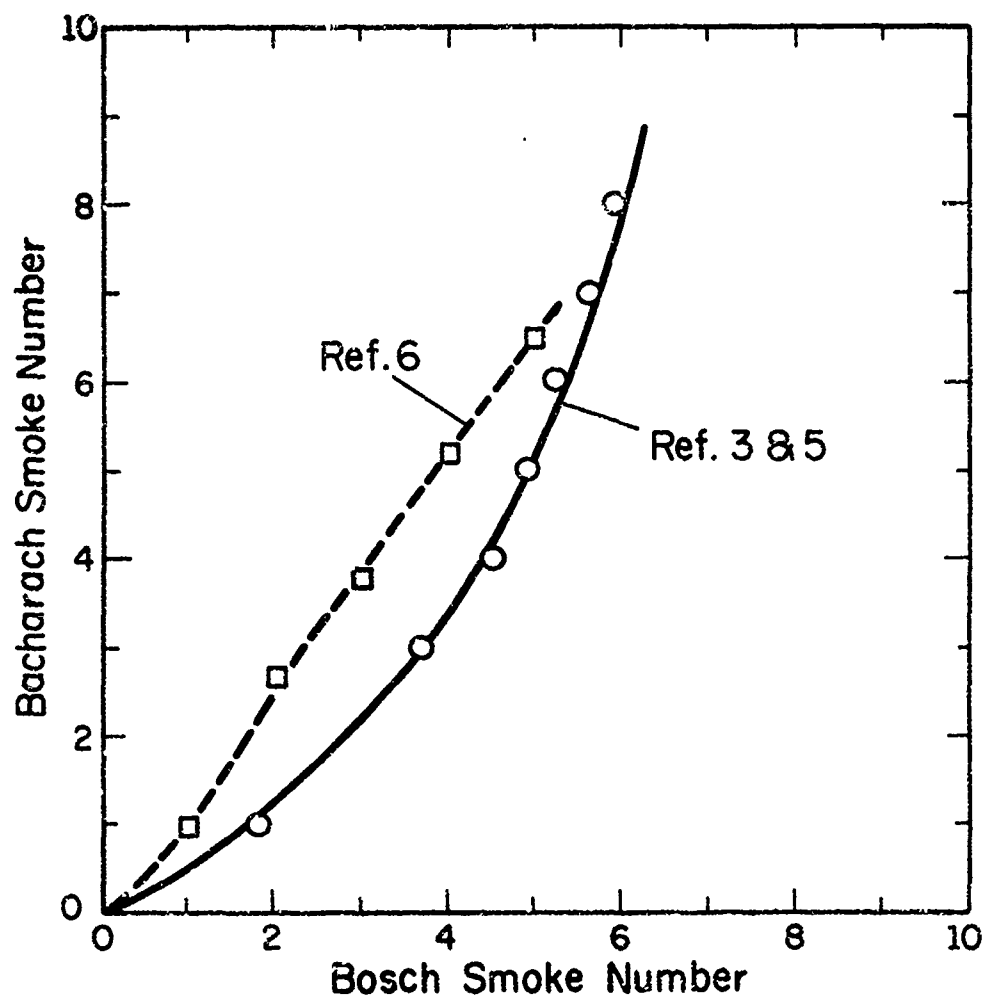


Figure 33 Correlation of Bacharach Smokemeter with Bosch Smokemeter

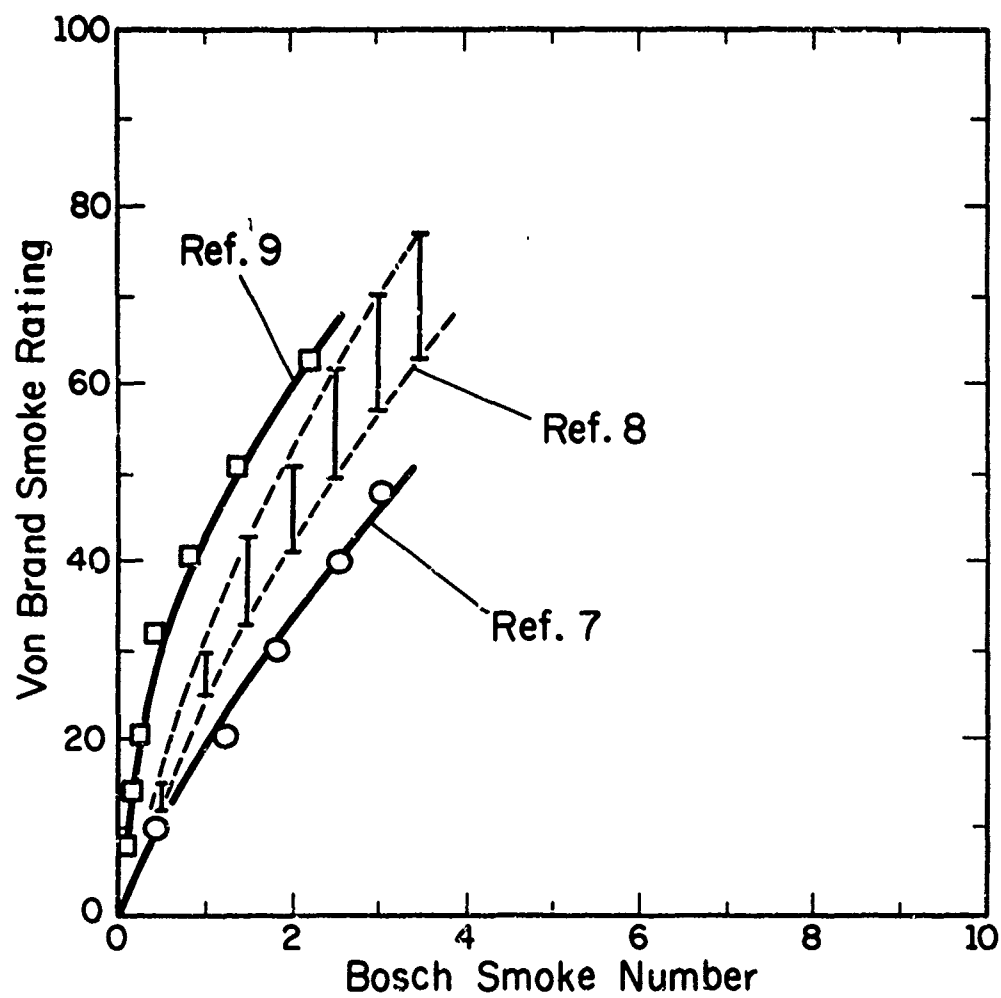


Figure 34 Correlation of Von Brand Smokemeter with Bosch Smokemeter

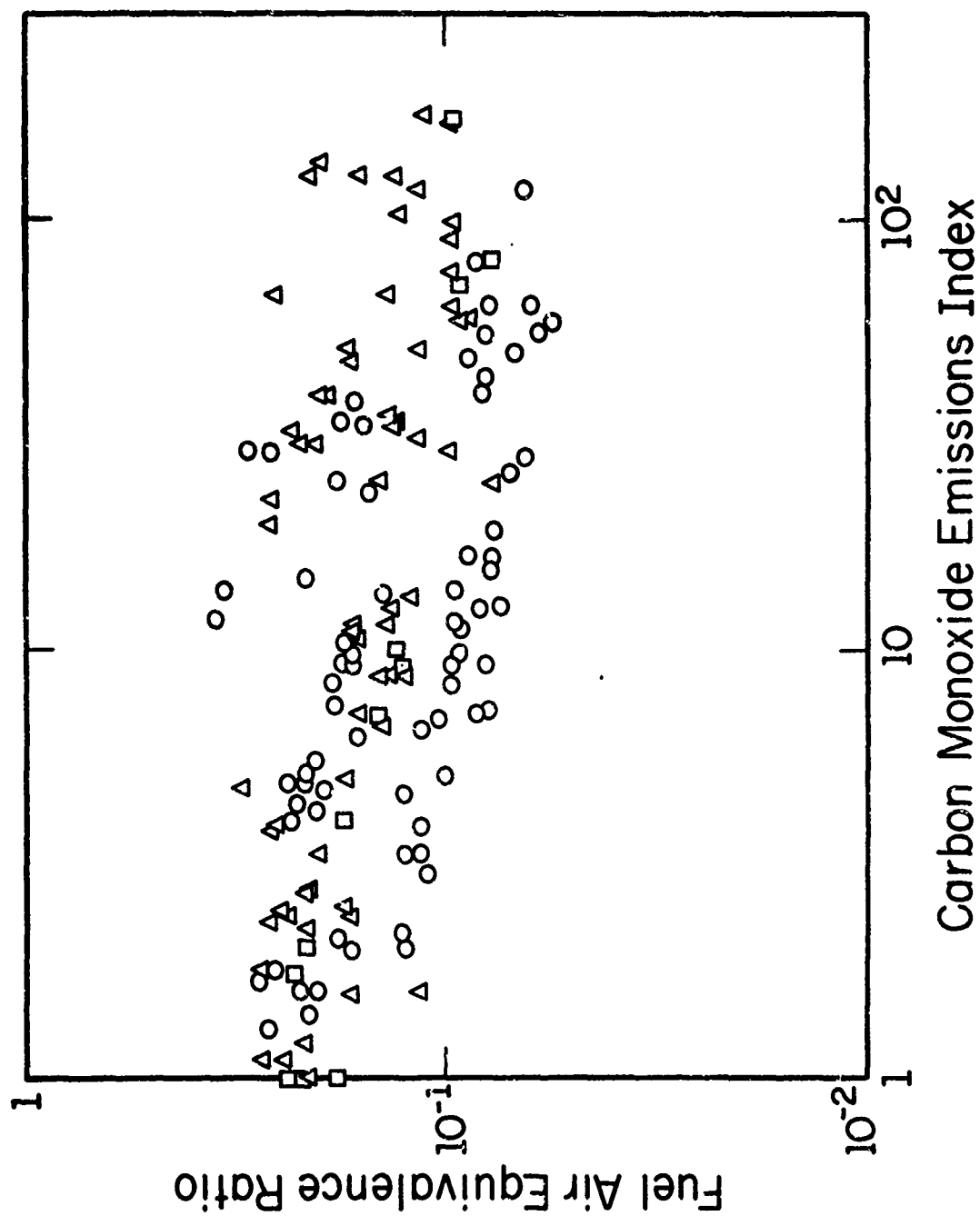


Figure 35 Carbon Monoxide Emission Index vs. Fuel Air Equivalence Ratio for Gas Turbines

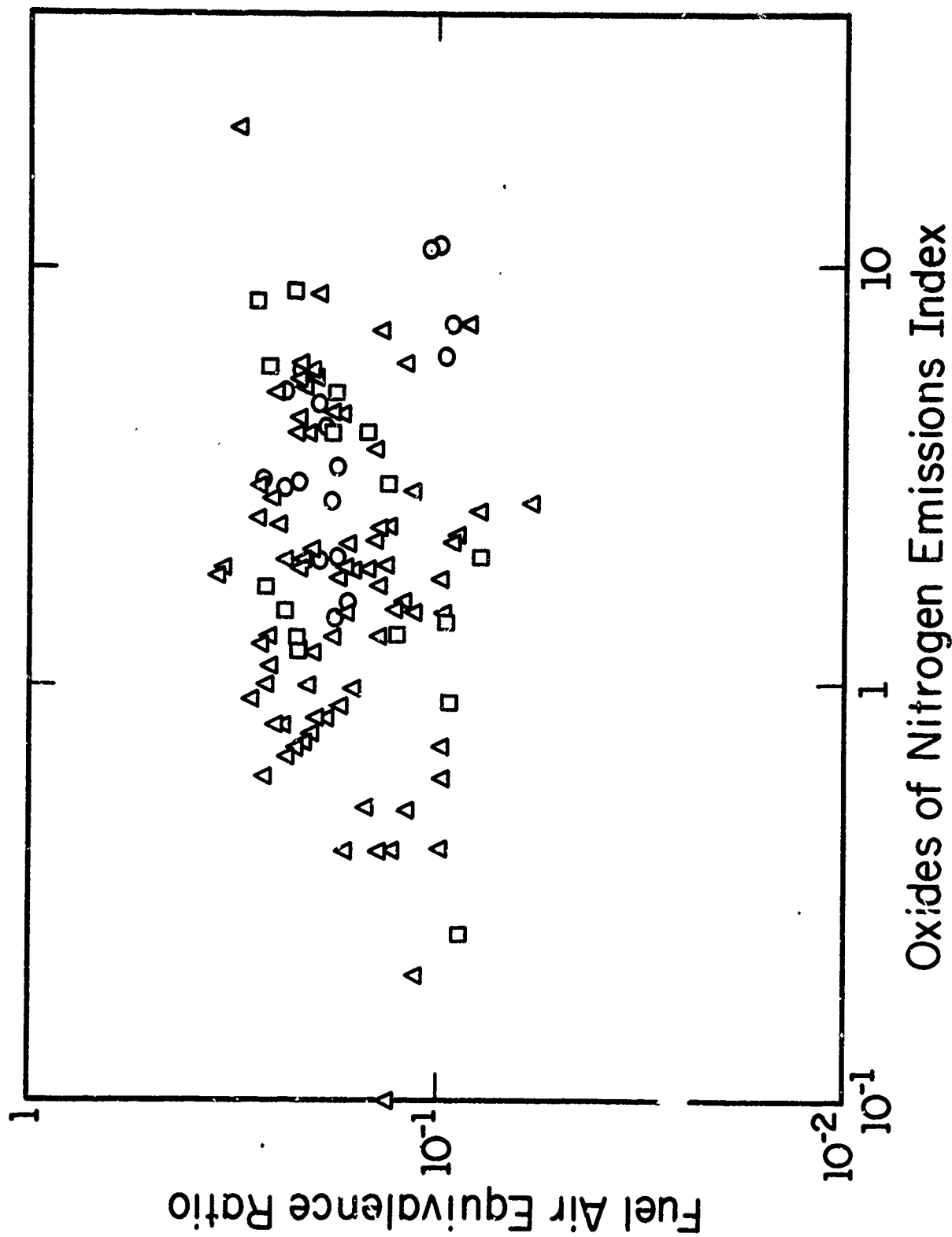


Figure 36 Oxides of Nitrogen Emissions Index vs. Fuel Air Equivalence Ratio for Gas Turbines

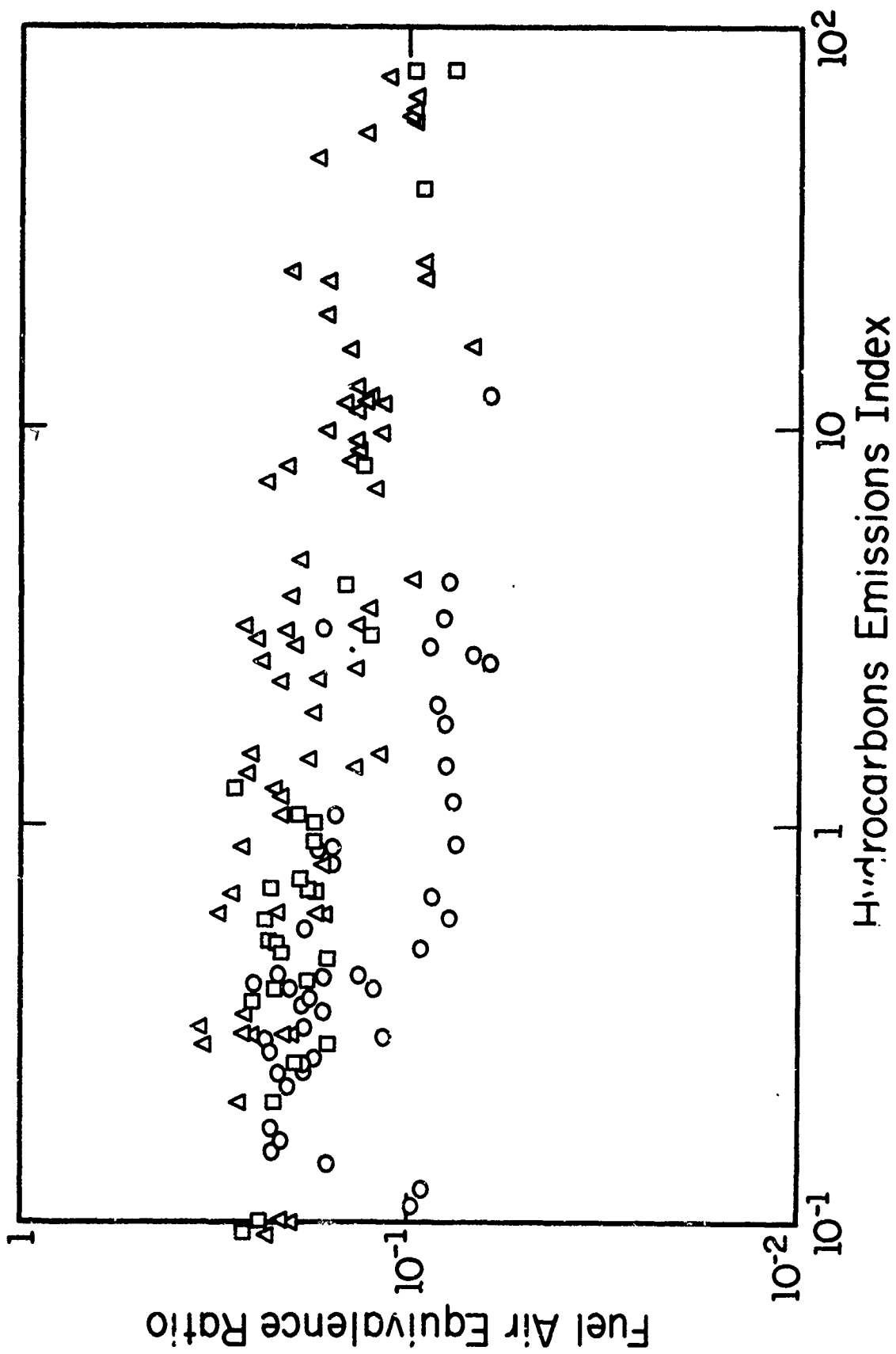


Figure 37 Hydrocarbon Emissions Index vs. Fuel Air Equivalence Ratio for Gas Turbines

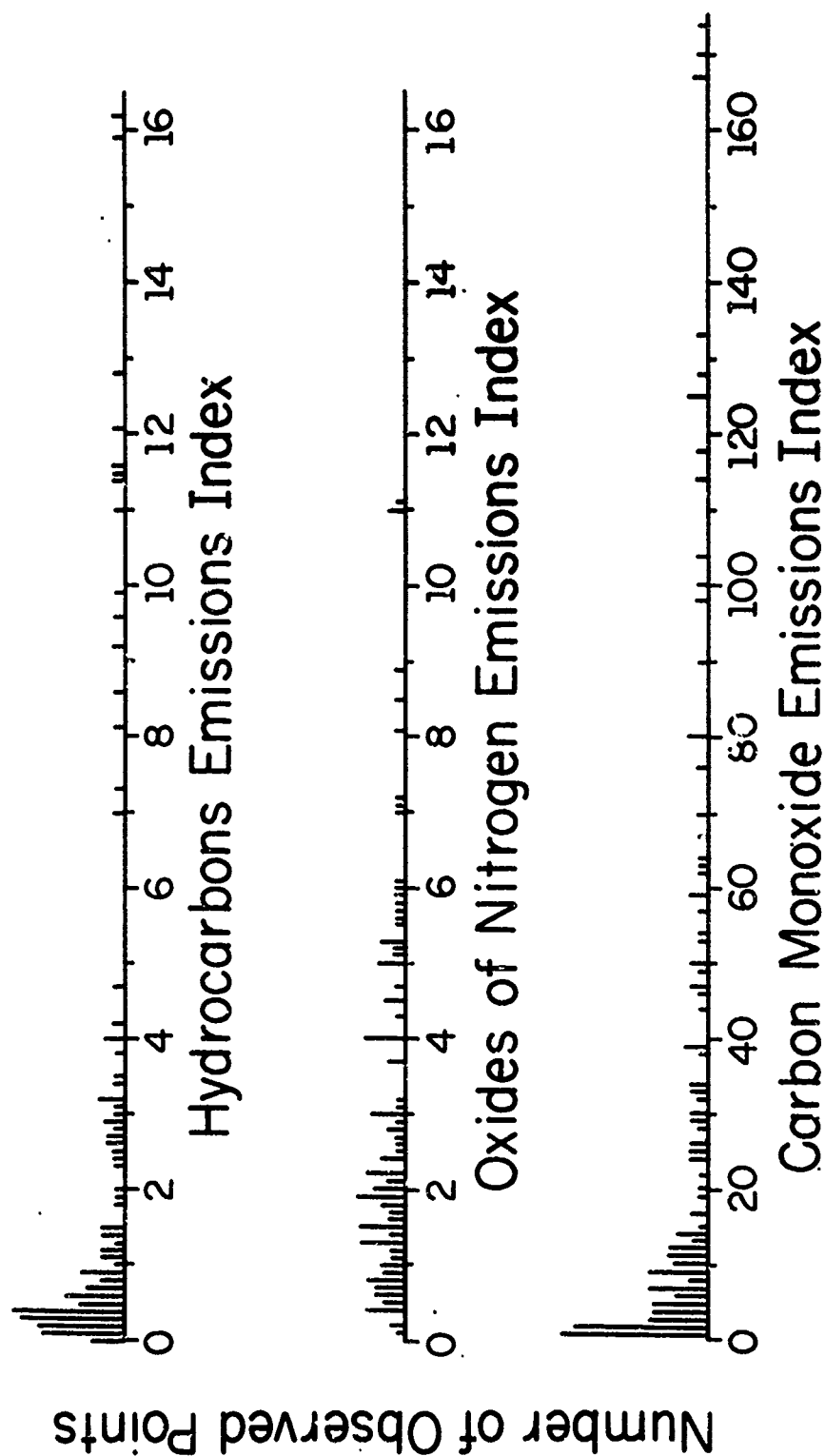


Figure 38 Frequency Distribution of Experimental Emission Indices for Gas Turbines

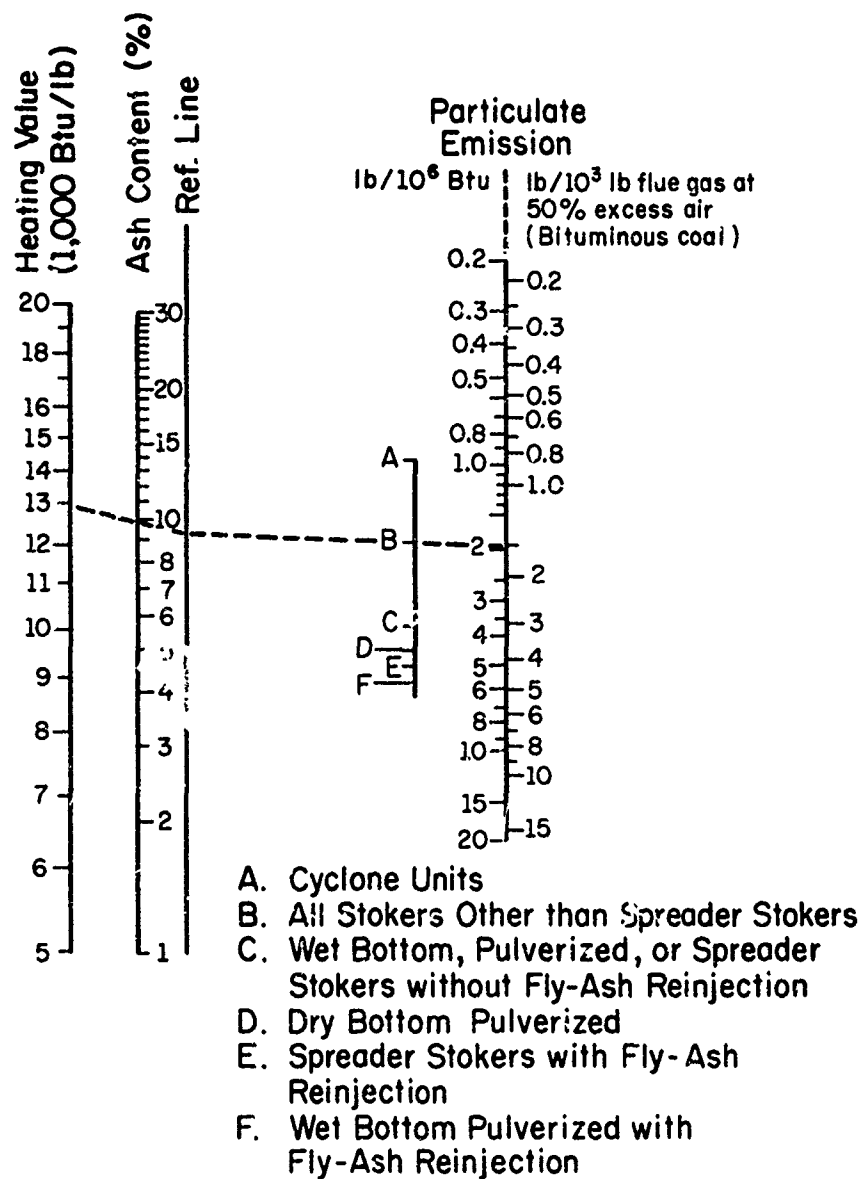


Figure 39 Nomograph for Estimating Particulate Emissions from Coal Combustion (without Air Pollution Control Equipment) (Ref. 22)

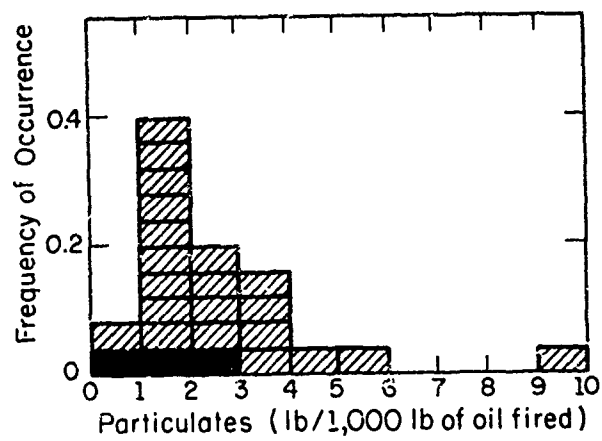


Figure 40 Particulate Emissions from Oil-Fired Small Sources (Ref. 23)

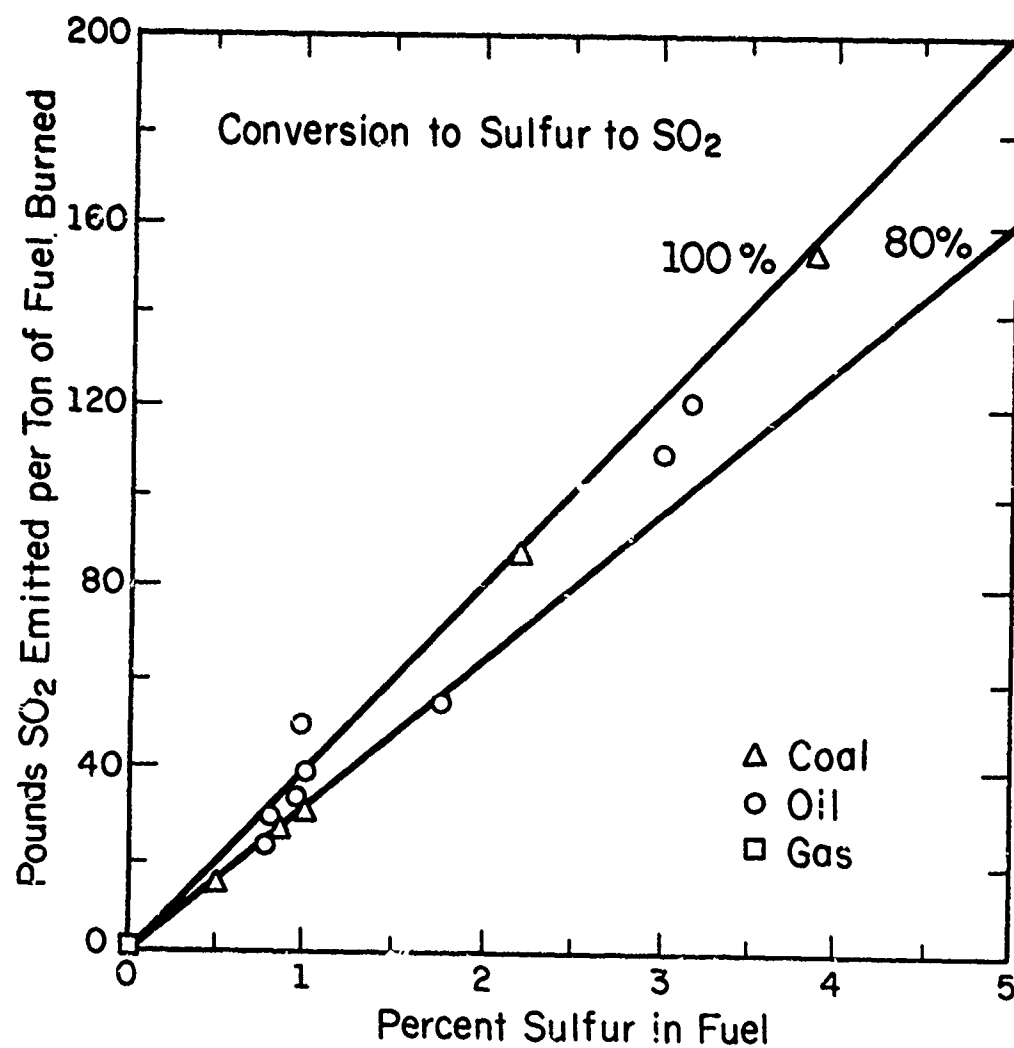


Figure 41 Sulfur Dioxide Emissions Compared with the Sulfur Content of Fuel

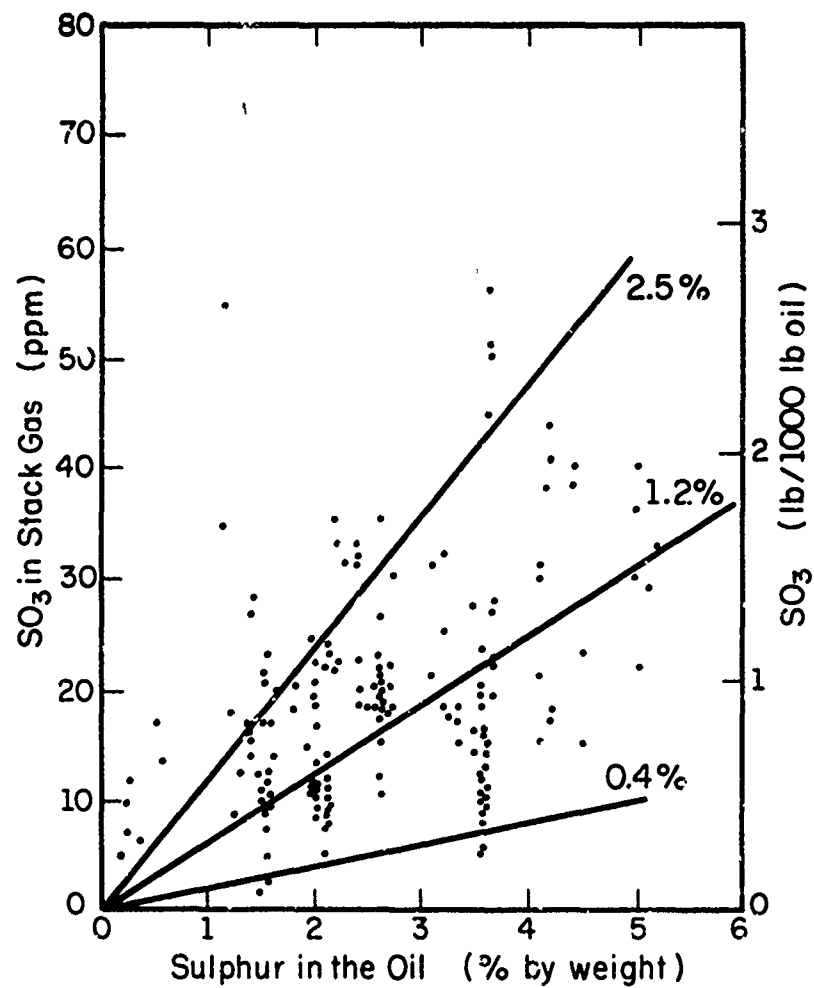


Figure 42 Relationship between SO₃ Emission and Sulfur in Oil (Ref. 23)

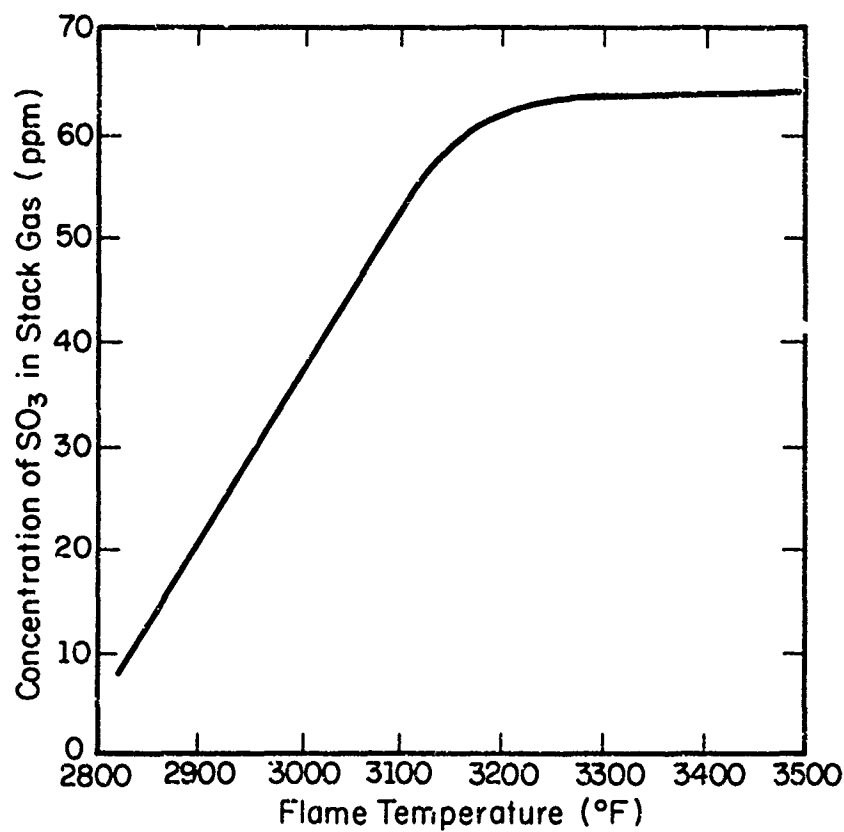


Figure 43 Effect of Flame Temperature on SO₃ Emission (Ref. 25)

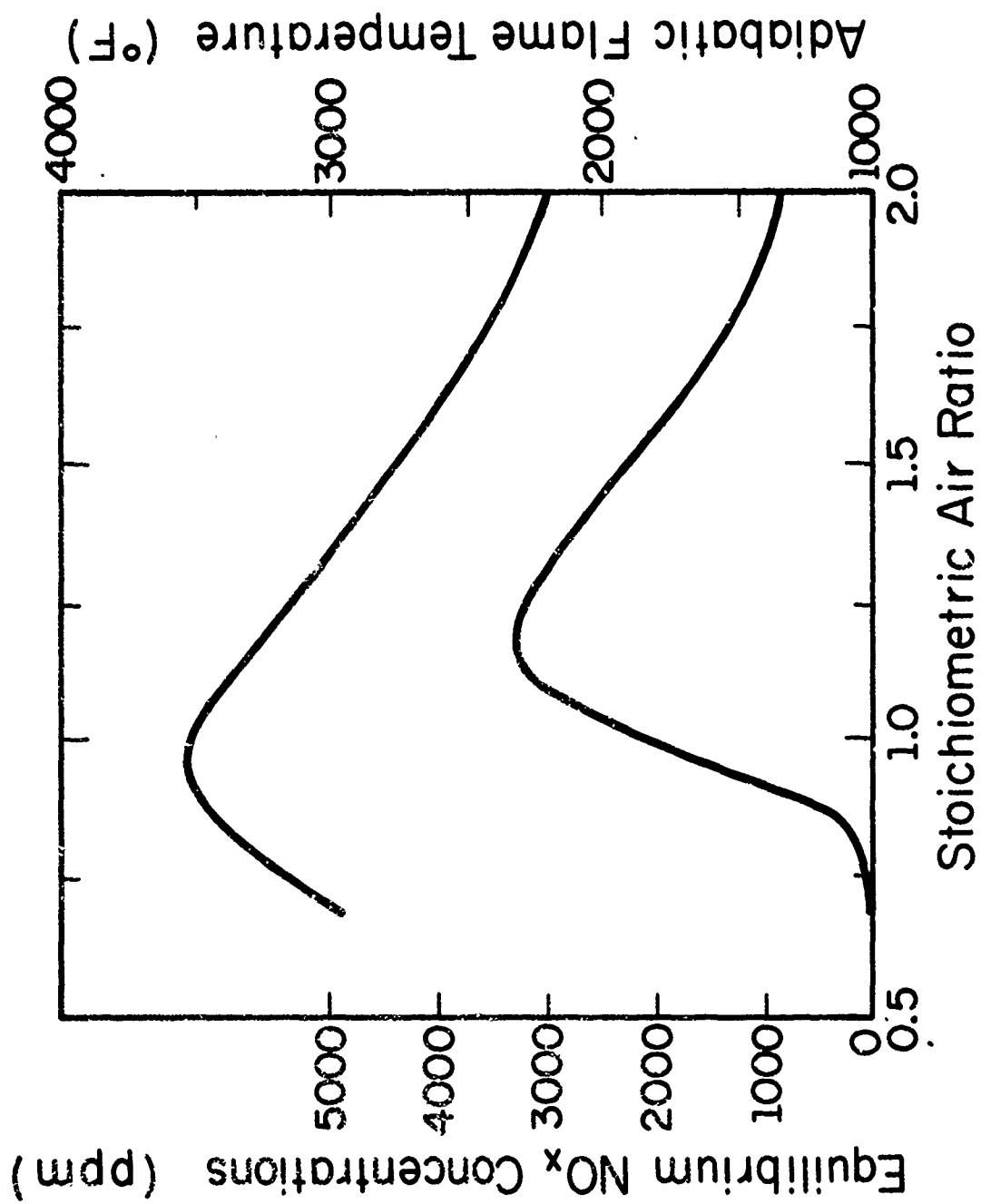


Figure 44 NO_x Equilibrium in Methane-Air Flames (Ref. 27)

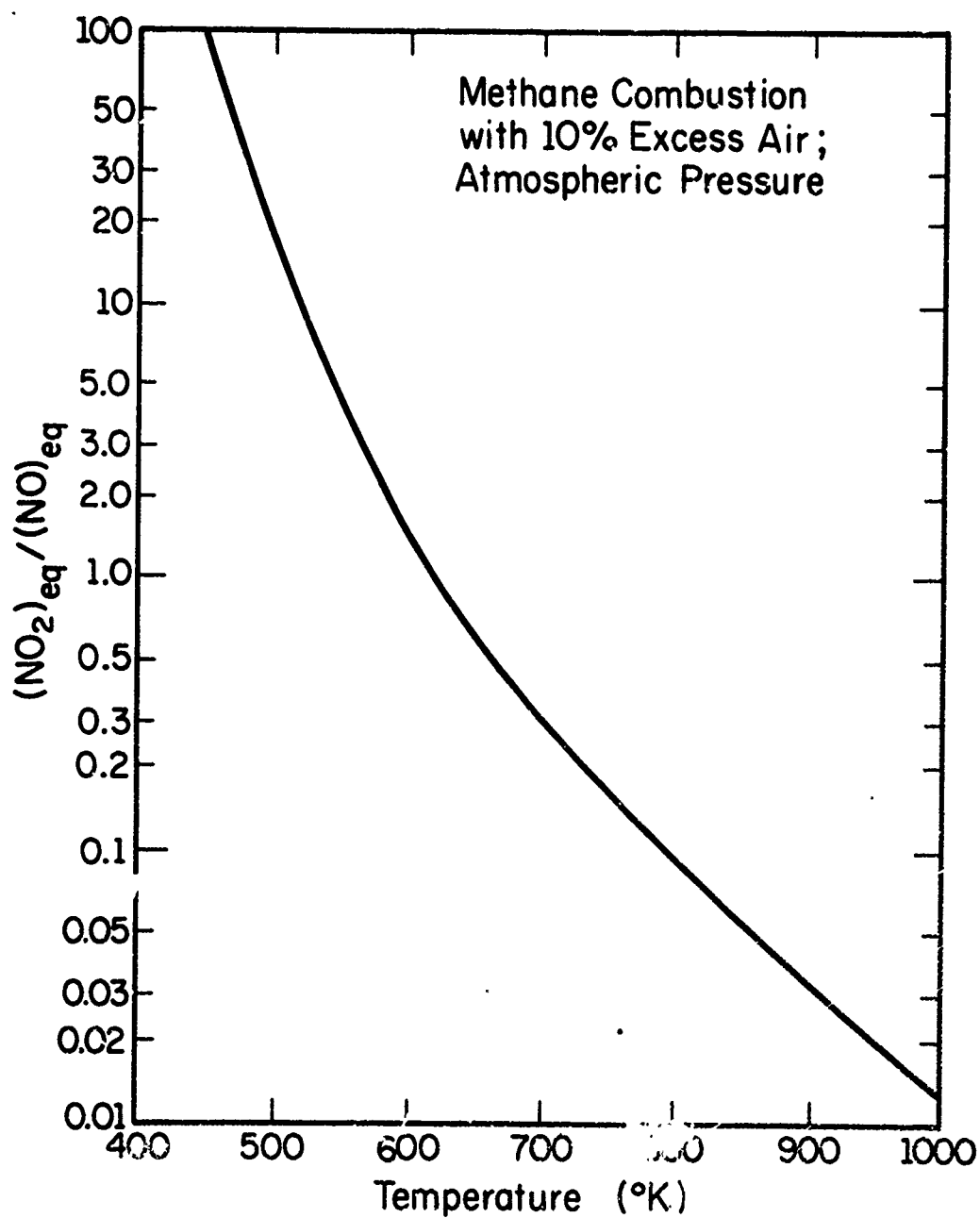


Figure 45 Equilibrium Concentrations of NO and NO₂ in Combustion Gases (Ref. 27)

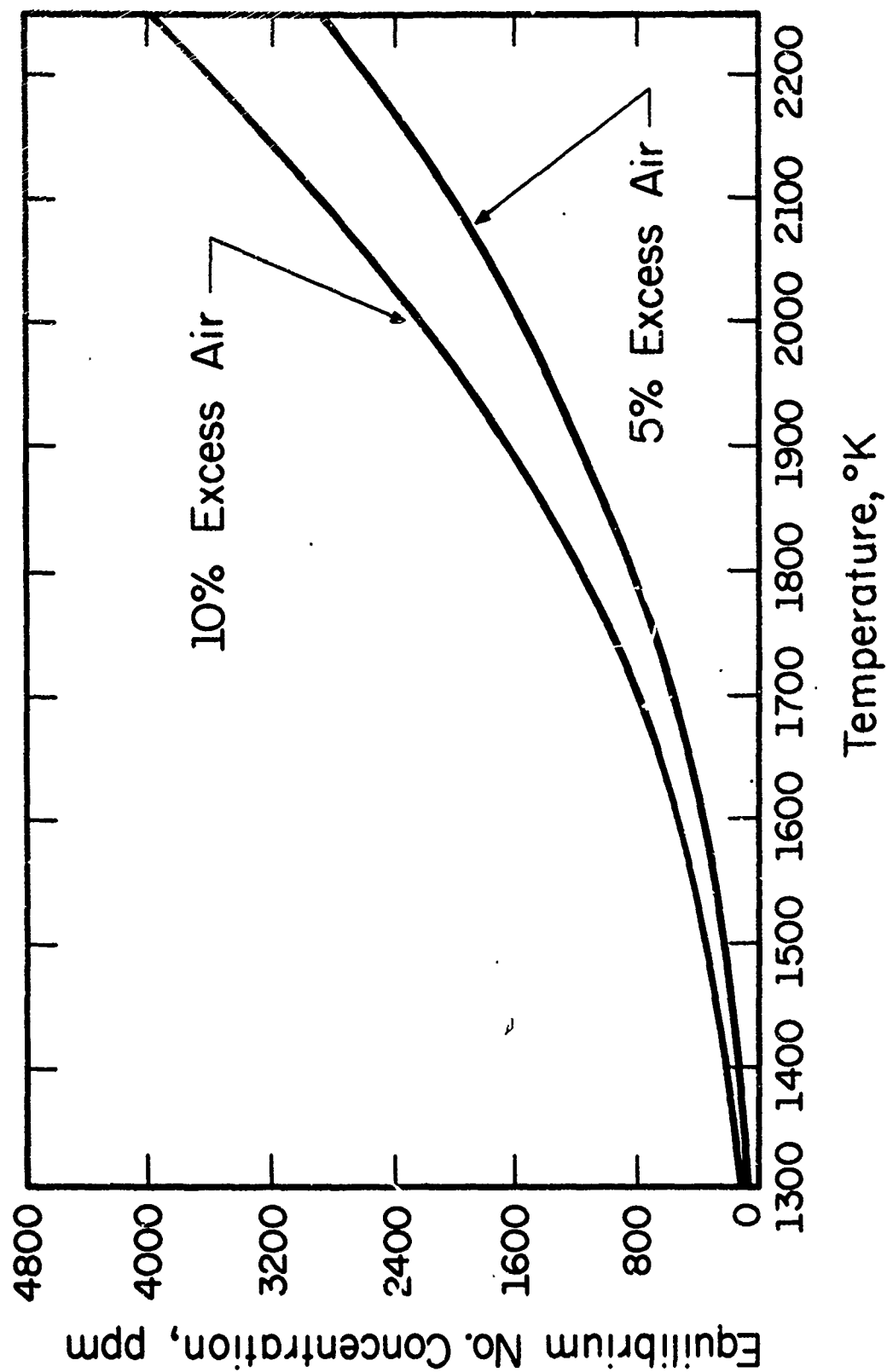


Figure 46 Equilibrium NO Concentrations for Combustion of Methane
(Ref. 27)

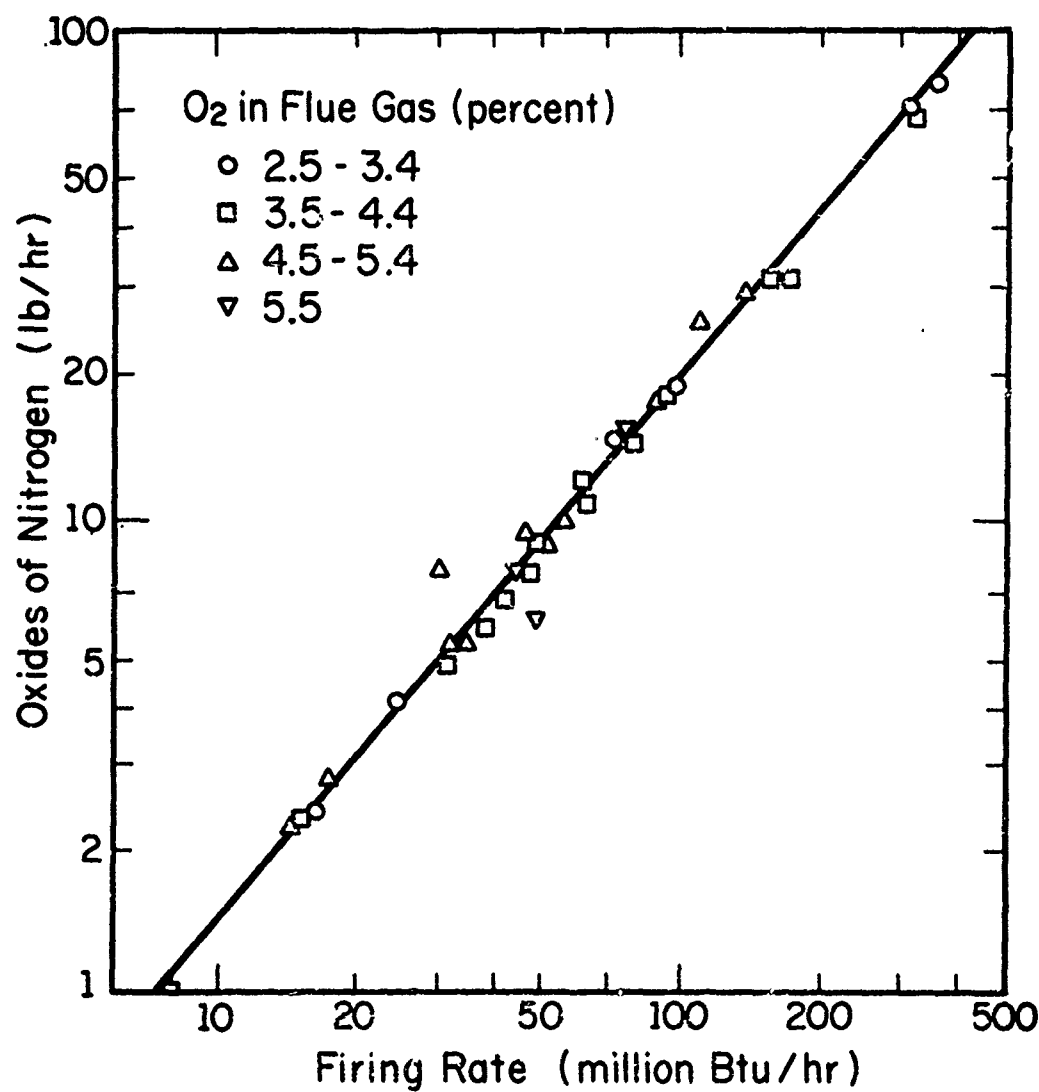


Figure 47 NO_x Emissions from Gas-Fired Refinery Furnaces (Ref. 27)

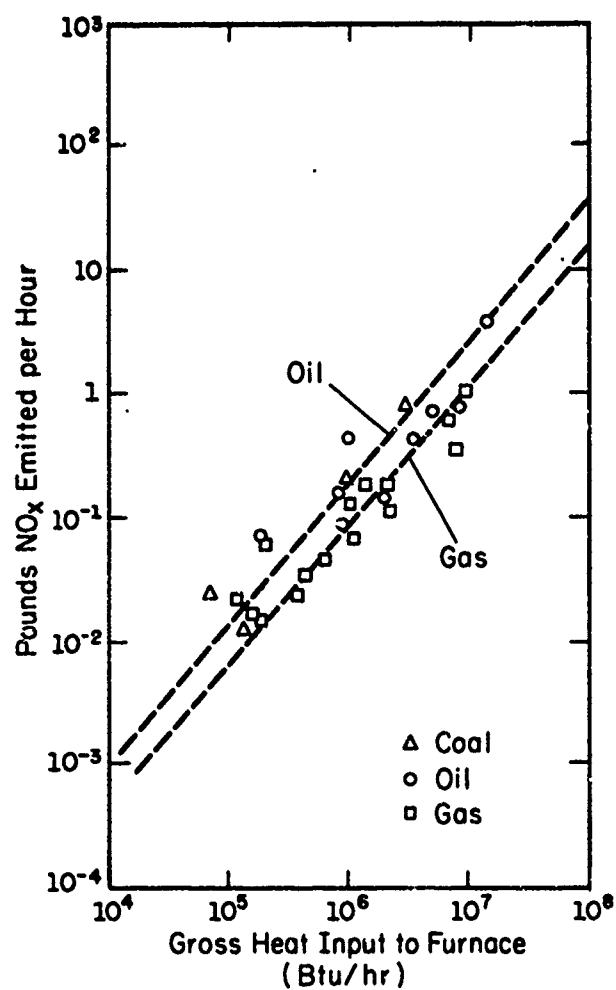


Figure 48 NO_x Emissions from Coal-, Oil-, and Gas-Fired Furnaces

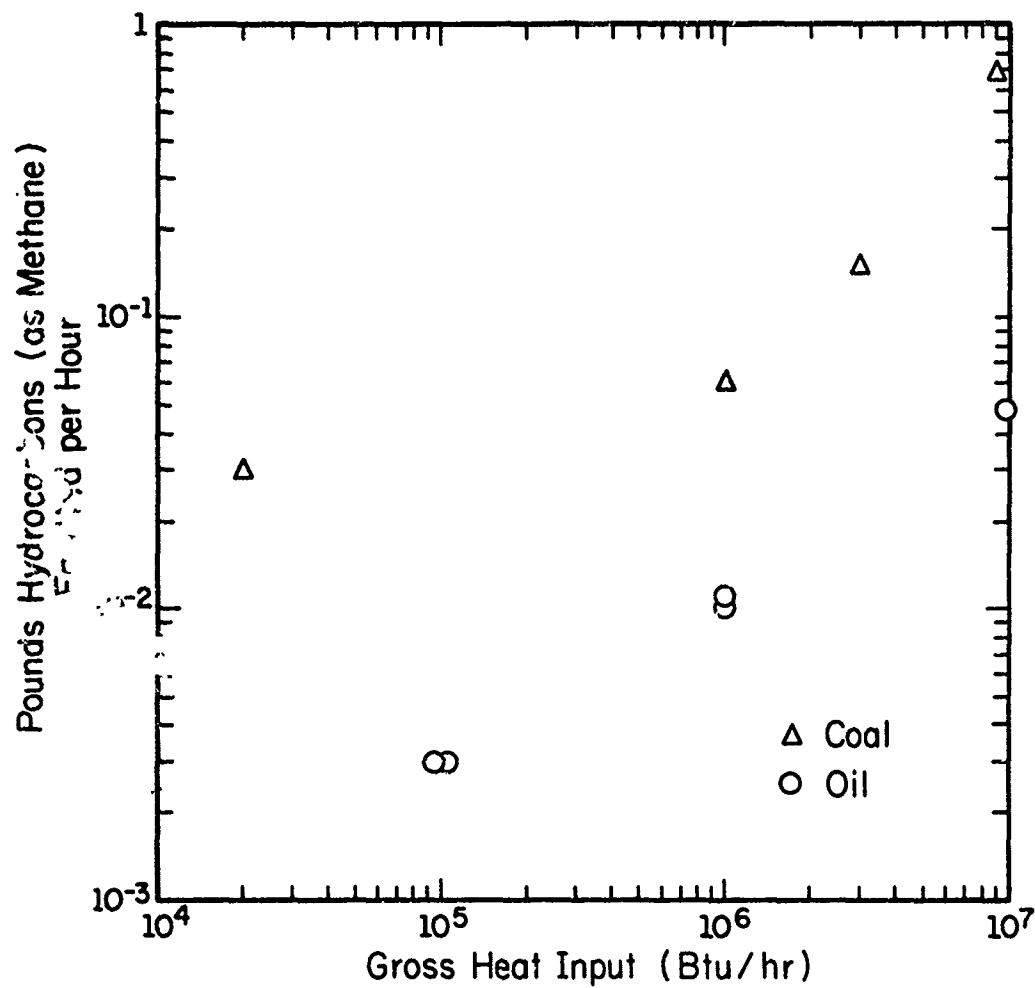


Figure 49 Hydrocarbon Emissions from Coal- and Oil-Fired Furnaces

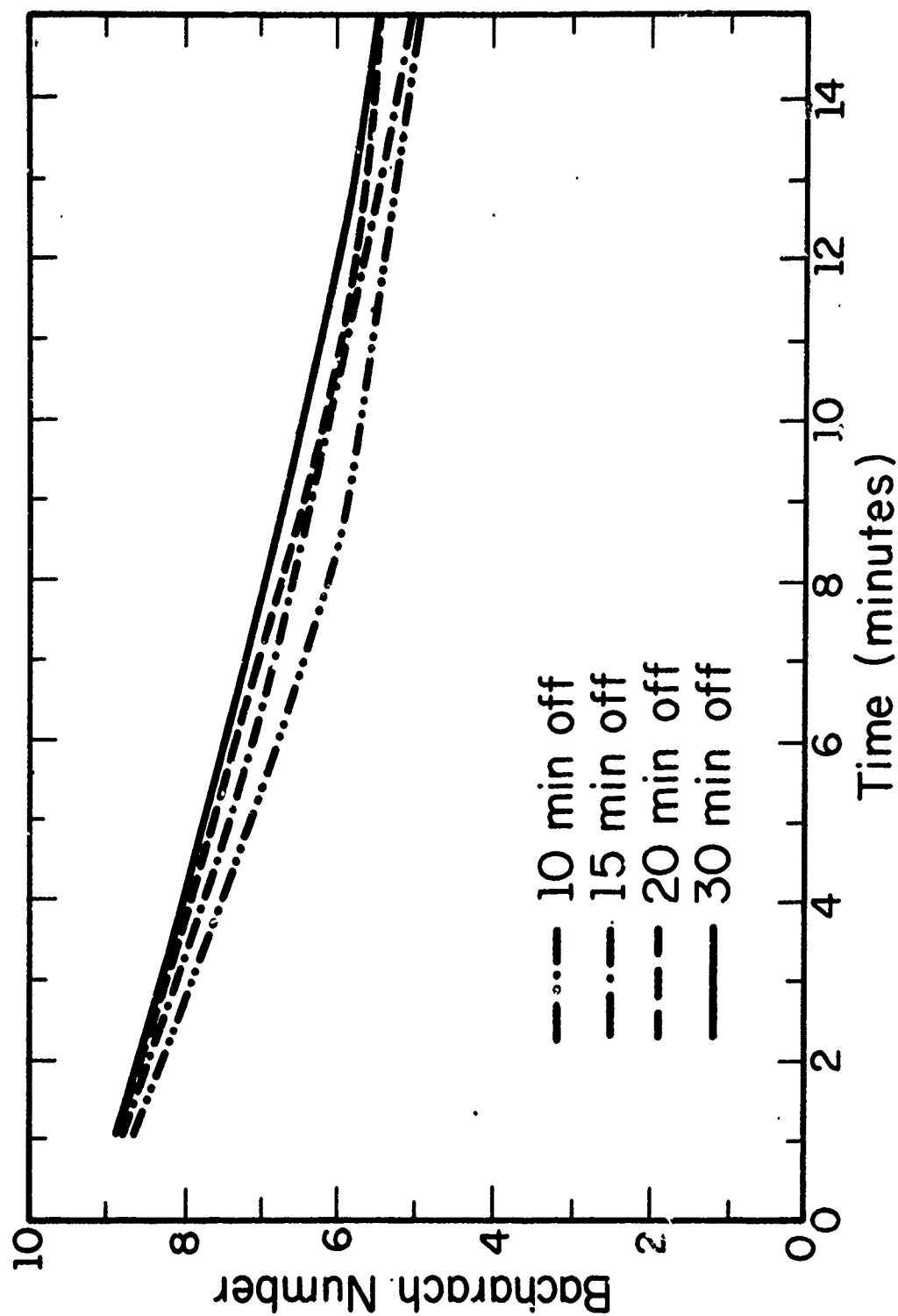


Figure 50 Smoke Emissions vs. Time for Varying On and Off Periods for Domestic Oil-Fired Heating Units (Ref. 31)

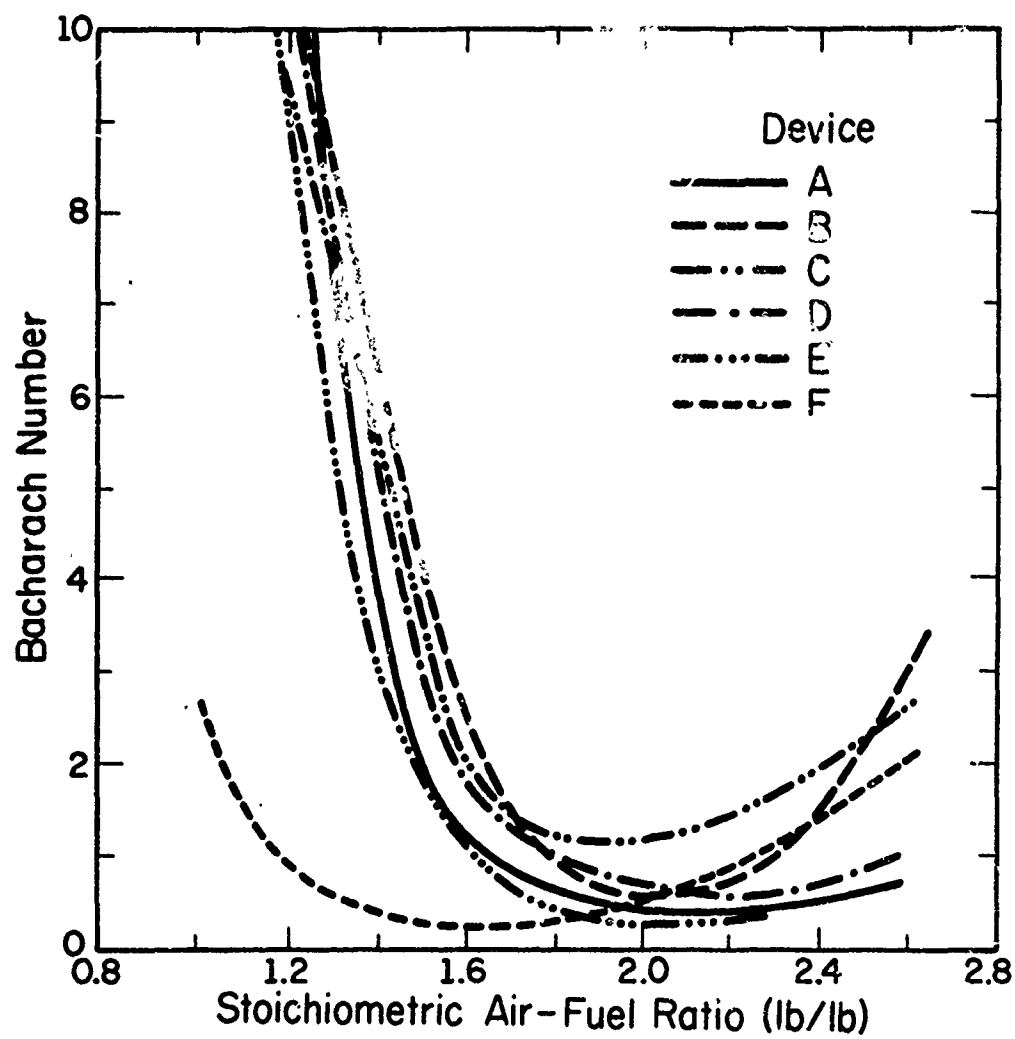


Figure 51 Average Smoke Emissions from Domestic Oil-Fired Heating Units (Ref. 31)

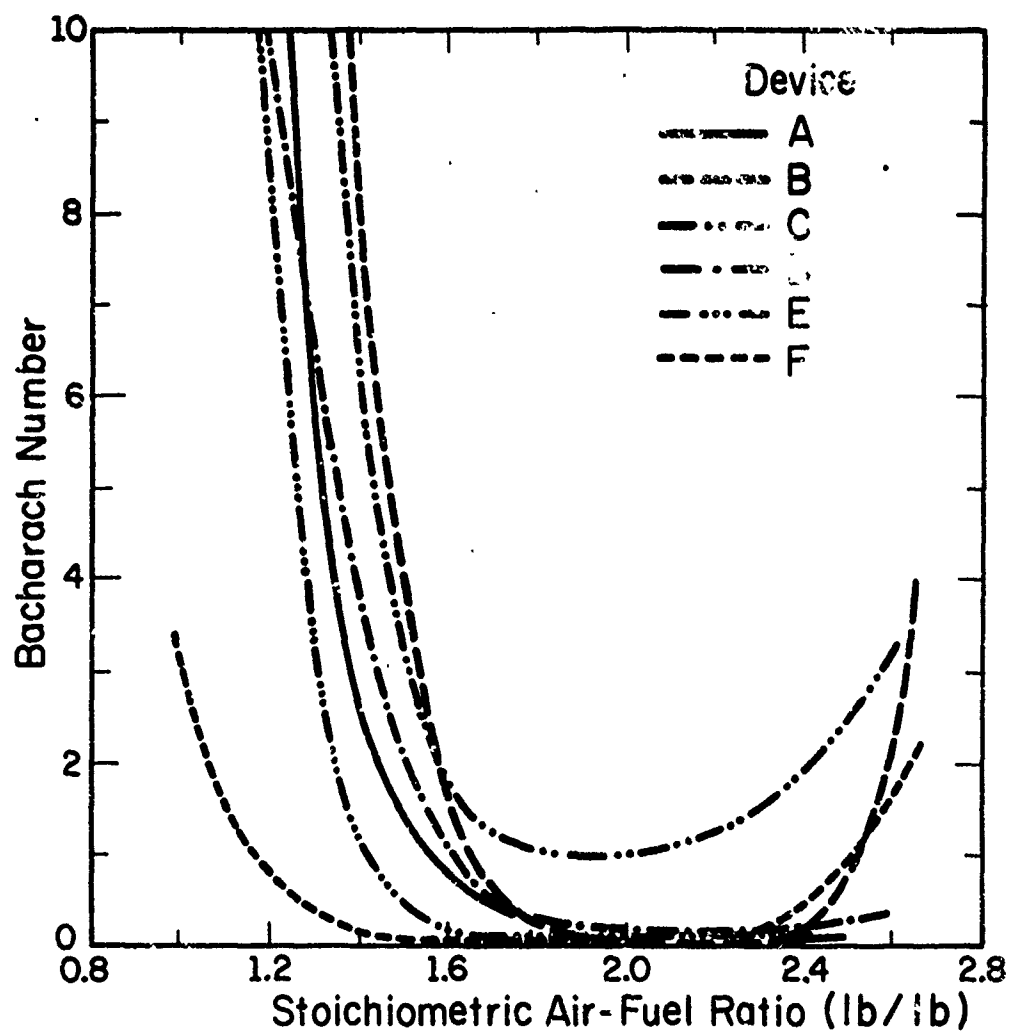


Figure 52 Tenth-minute Smoke Emissions from Domestic Oil-Fired Heating Units (Ref. 31)

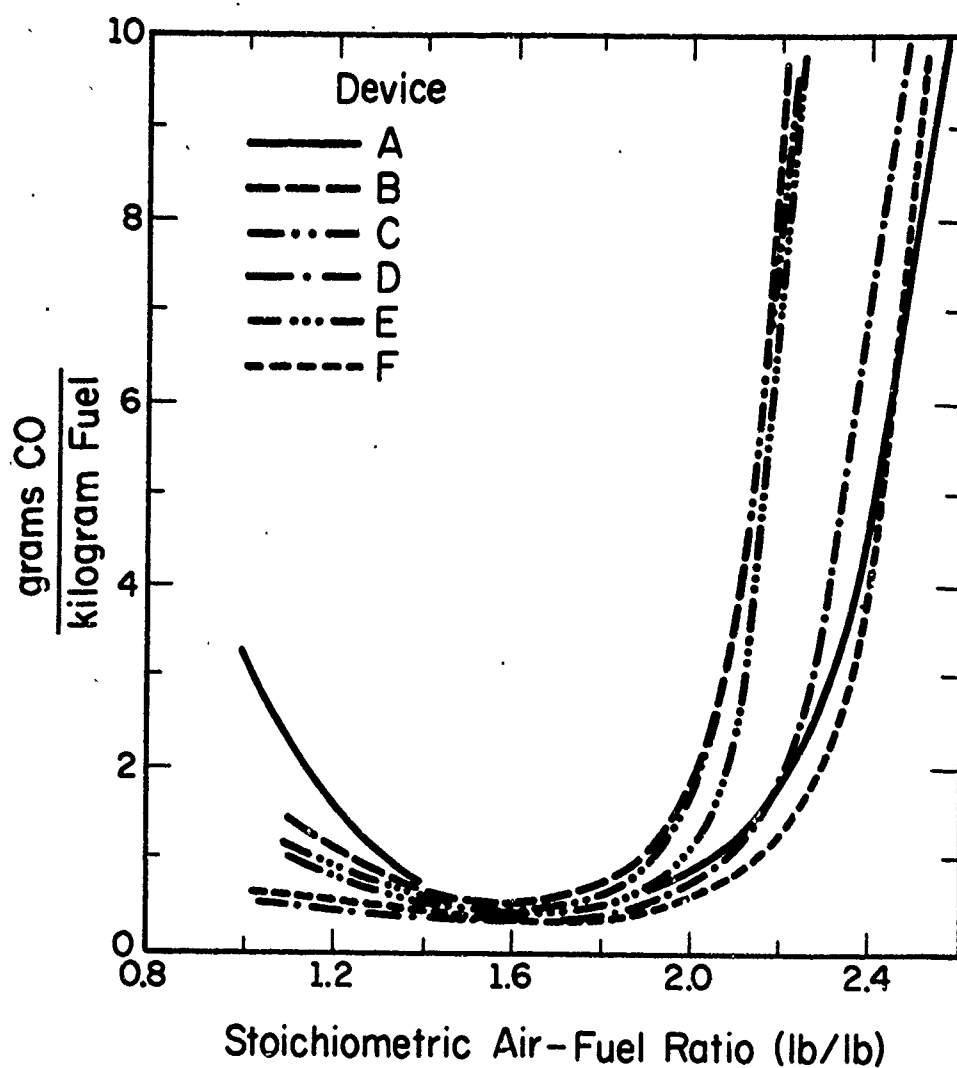


Figure 53 Carbon Monoxide Emissions from Domestic Oil-Fired Heating Units (Ref. 31)

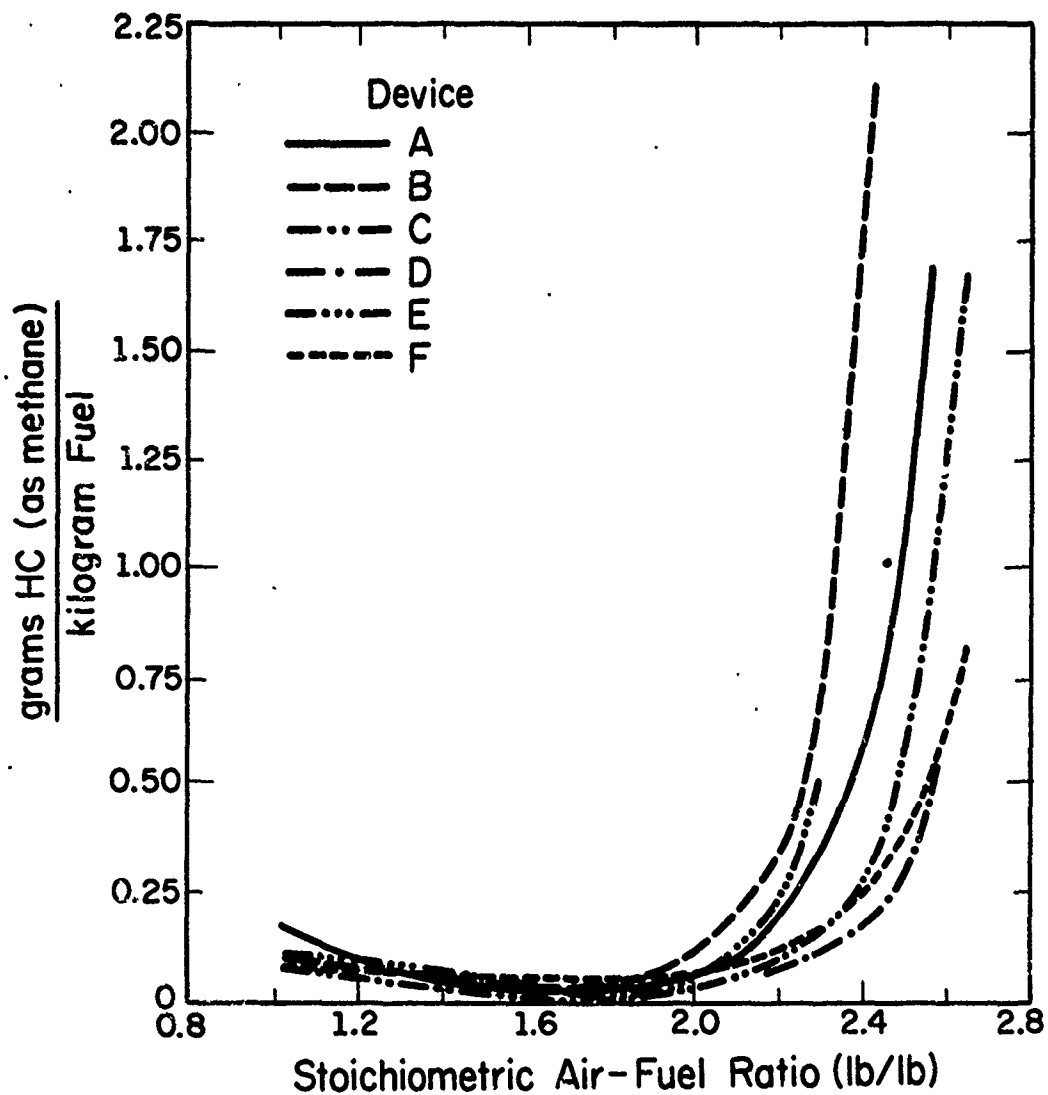


Figure 54 Gaseous Hydrocarbon Emissions from Domestic Oil-Fired Heating Units (Ref. 31)

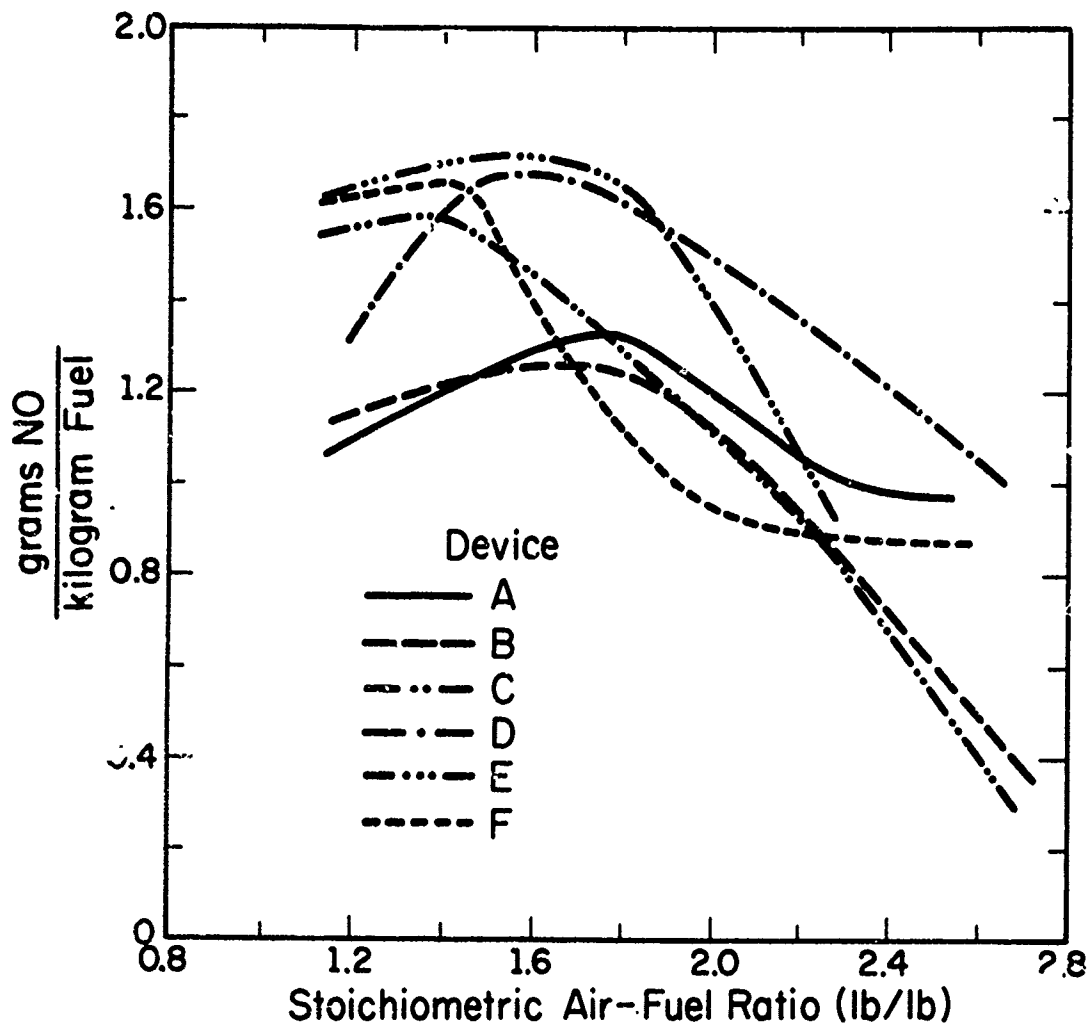


Figure 55 Nitrogen Oxide Emissions from Domestic Oil-Fired Heating Units (Ref. 31).

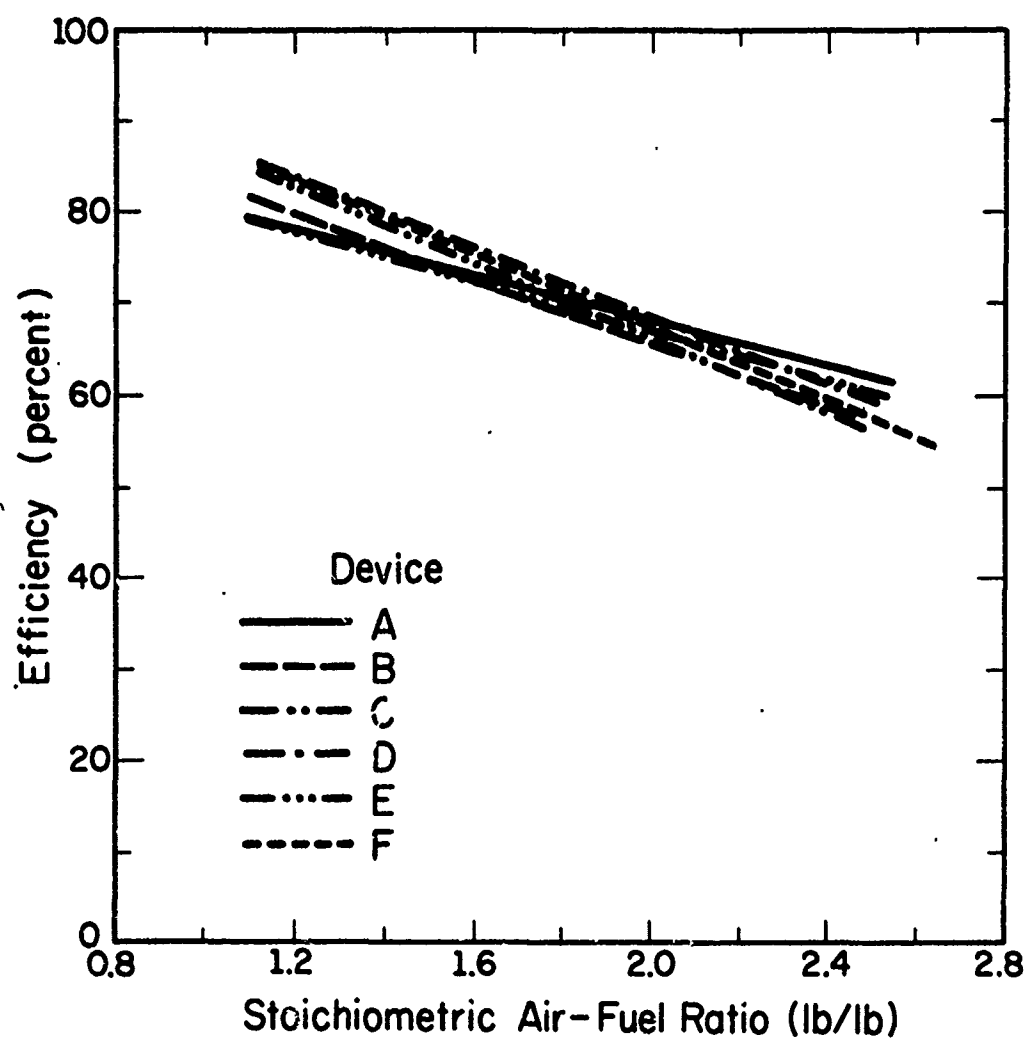


Figure 56 Overall Heating Efficiencies from Domestic Oil-Fired Heating Units (Ref. 31)